CRITICAL CONSTANTS

by

CHARLES VOWLES

M. Eng.
of
University of Liverpool, England

SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE
in
Chemical Engineering

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
(1951)

Signature of Author _____
Dept. of Chem. Engr., May 18, 1951

Certified by _____
Thesis Supervisor

_____
Chairman, Departmental Committee on Graduate Students

CRITICAL CONSTANTS

by

Charles Vowles

Submitted for the degree of Master of Science in the Department of Chemical Engineering on May 18, 1951

ABSTRACT

A method of predicting critical constants of substances is presented which requires a knowledge only of the structural formulae of the substances concerned together with a series of elemental values for each of the three cases of critical volume, critical temperature and critical pressure. These elemental values have been determined and are presented.

In the critical volume case, the elemental values for all the atoms and structural elements in the molecule concerned are added to give the critical volume of that compound. For critical temperatures, the summation of the elemental values gives the ratio of the normal boiling temperature to the critical temperature of the compound concerned. Since normal boiling temperatures are quoted in the literature for a wide range of substances, the critical temperature can be obtained from this ratio. The summation of the elemental values in the critical pressure case gives the ratio of the critical temperature to the critical pressure raised to a power "a". This exponent, constant for any series, is determined for the most common cases and together with it and the critical temperature, the critical pressure for the compound concerned may be obtained.

The predictions may be expected to be within five per cent for critical volumes, three per cent for critical temperatures and ten per cent for critical pressures when organic substances are involved. Accurate predictions for inorganic substances are given only in the critical temperature case.

Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge 39, Massachusetts

May 18, 1951

Professor Joseph S. Newell
Secretary of the Faculty
Massachusetts Institute of Technology
Cambridge 39, Massachusetts

Dear Sir:

I herewith submit the thesis entitled "Critical Constants" in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering.

Yours respectfully,

Charles Vowles

ACKNOWLEDGEMENT

The author wishes to express his appreciation to Professor Meissner of the Chemical Engineering Department for the very great interest he has shown in this work and for his extremely helpful suggestions.

TABLE OF CONTENTS

LIST OF TABLES

List of Tables (cont)

List of Tables (cont)

LIST OF GRAPHS

List of Graphs (cont)

SUMMARY

I SUMMARY

A method for predicting critical constants of substances is presented which requires a knowledge only of the structural formulae of the substances concerned together with a series of elemental values, given below, for each of the three cases of critical volume, critical temperature and critical pressure. It is shown that:

$$\text{Molal critical volume} = V_c = \sum p\,X \text{ (ccs./grm. mol)}$$

$$\frac{\text{Normal boiling temperature}}{\text{Critical temperature}} = \frac{T_b}{T_c} = \sum q\,Y \text{ (dimensionless)}$$

$$\frac{\text{Critical temperature}}{(\text{Critical pressure})^a} = \frac{T_c}{P_c{}^a} = \sum r\,Z \text{ (°K/atmos}^a\text{)}$$

where X, Y, Z are values assigned to each atom and structural element for the cases of critical volume, temperature and pressure respectively.

p, q, r are the numbers of atoms or structural elements in the molecules corresponding to X, Y and Z respectively.

Thus, if a substance contains x atoms of A, y atoms of B and z double bonds, then:

$$V_c = x\,X_A + y\,X_B + z\,X_{DB}$$

The values of X, Y and Z for the various atoms and structural elements have been determined from the experimental data available and are presented below in Table 1.

With critical volumes, the errors for the sixty-three organic compounds considered were less than four per cent in ninety per cent of the cases, the maximum error being seven

per cent. Accurate predictions were not made generally for the elements and inorganic compounds.

For critical temperatures, in the one hundred and thirty organic compounds considered, a maximum error of 5.50% was encountered, the error in ninety-five per cent of the cases lying within three per cent. With inorganic compounds and elements, good accuracy was obtained, the average deviation for nineteen cases being 3.30% and the maximum 7.50%.

A series of elemental values, universally applicable to all compounds, was obtained for critical pressures. The exponent "a", though constant and equal to 0.80 for the paraffin hydrocarbons, olefins, aromatics, esters, ethers, amines, halogen-substituted hydrocarbons, sulfides and mercaptans, differed for several homologous series and was found to be 0.65 for the alcohols, 0.68 for the nitriles, 0.685 for the carboxy acids and 0.665 for the phenols. In eighty per cent of the one hundred organic compounds considered, the error was less than five per cent, while in ninety-five per cent of the cases, it was less than ten per cent. The maximum error encountered was seventeen per cent. The method proved to be unreliable for elements and inorganic compounds.

Data for compounds containing more than eight carbon atoms are not available and thus the method presented could not be checked beyond this range, but prediction within this range is good and is recommended where no experimental data are available.

Table 1

Values of X, Y and Z for the Atoms and Structural Elements

Element	Symbol	Critical Volume X	Critical Temp. Y	Critical Pressure Z
Carbon	C	23.0	-0.5592	1.02
Hydrogen	H	17.0	0.2875	1.95
Hydroxyl Group	(OH)	38.0	0.3382	23.10
Oxygen	O	21.0	-0.0165	3.00
Nitrogen	N	13.5	-0.2625	2.45
Sulfur	S	58.0	0.0140	6.70
Fluorine	F	33.0	0.3042	3.63
Chlorine	Cl	63.5	0.2983	7.45
Bromine	Br	82.7	0.2990	9.38
Iodine	I	110.9	0.2994	10.95
Double Bond (C=C)	D_{cc}	13.2	0.5640	2.50
Double Bond (C=O)	D_{co}	18.0	0.5640	2.50
Double Bond (C=S)	D_{cs}	18.0	0.5640	2.50
Double Bond (S=O)	D_{so}	18.0	0.5640	2.50
Triple Bond (C≡C)	T_{cc}	32.7*	1.1415	5.59*
Triple Bond (C≡N)	T_{cn}	60.5	1.1590	29.10
Triple Bond (N≡N)	T_{nn}	60.5	1.1590	2.68*
Six membered ring (Aromatic and Naphthenic)	R_6	-22.5	0.5666	-0.14

* Values calculated from single compounds.

INTRODUCTION

II INTRODUCTION

The Critical Temperature of a substance may be defined as the minimum temperature above which the substance cannot be liquified by the application of pressure, no matter how great it may be. As the temperature of a substance is raised towards its critical, the density of the liquid phase decreases and that of the saturated vapor phase increases until at the critical point the meniscus separating the phases flattens and disappears and the properties of the two phases become identical. The saturated vapor pressure at this temperature is called the Critical Pressure, the density, the Critical Density and the specific volume, the Critical Volume. Direct methods of determining these critical constants experimentally are discussed briefly in Appendix A and the list of experimental values are presented in Appendix B.

Several important methods for prediction and correlation of the pressure-volume-temperature relations for liquids and gases, heats of vaporization, surface tensions, etc., require a knowledge of the critical constants of the substances concerned. While experimentally determined values are reported in the literature for many substances, in the majority of cases they are not known since determination is not simple and in many cases is impossible due to decomposition of the substance before the critical point is reached.

Thus it is important that reliable methods of prediction be available. The ideal is a single relationship for each

of the three constants in terms of easily measurable physical properties giving values for each substance. Much work has already been done in this direction and many empirical relations exist (see Appendix C). In almost all cases, the relations developed apply only to limited groups or series of compounds or else they contain constants which are constant for only one group or series but which vary from group to group.

In recent years, much of the work done has involved the parachor and molar refraction as parameters and equations have been proposed in terms of these properties which satisfy with reasonable limits of accuracy the majority of existing experimental values.

Sugden (59) defined the parachor of a substance:

$$\text{Parachor} = [P] = M\gamma^{1/4}/(D - d) \qquad (1)$$

where M = Molecular weight
γ = Surface tension in dynes/cm.
D = Liquid density in grms./cc.
d = Vapor density in grms./cc.

- all terms being measured at the same temperature and at the saturation pressure.

He showed that the parachor is substantially independent of temperature and that furthermore parachor values can be computed directly from the structural formulae of the compounds concerned by use of atomic and structural parachor values and without recourse to equation (1). These values are set out by Mumford and Philips (47) and revised values are given by Gibling (23). The more important atomic and structural

parachor values are given in Appendix D. An example will illustrate the simplicity of the calculation:

Toluene has seven carbon atoms, eight hydrogen atoms, three carbon to carbon double bonds and one six-membered ring, the parachors for these elements being 9.20, 15.40, 19.00 and 0.80 respectively. The parachor calculated for toluene is thus:

Parachor = 7 x 9.2 + 8 x 15.4 + 3 x 19.0 + 1 x 0.8 = 245.4

The observed value for this compound, obtained from equation (1) is 245.5. In general, agreement to within one per cent of the observed value is possible by this method.

Lorentz and Lorenz (38) have shown by means of the electromagnetic theory of light that the specific refraction may be represented as follows:

$$r_\lambda = \frac{1}{D}\left(\frac{n_\lambda^2 - 1}{n_\lambda^2 + 2}\right) \qquad (2)$$

where r_λ = Specific refraction
n_λ = Refractive index measured with monochromatic light of wave-length λ.
D = Density of liquid in grms./cc.

- all being measured at the same temperature.

The Molar refraction is defined:

$$[R_\lambda] = M\, r_\lambda = \frac{M}{D}\left(\frac{n_\lambda^2 - 1}{n_\lambda^2 + 2}\right) \qquad (3)$$

The molar refraction is independent of temperature and can be shown to be equal to the volume of the molecules of the substance if the wave-length of the monochromatic light used

approaches infinity. Measurements of refractive indices are difficult with light of long wave-length (infra-red) and generally they are measured with monochromatic light of the visible spectrum, usually of the sodium D line. Thus, while not giving the actual volume of the molecules, $[R_D]$ can be considered as a comparison of such volumes. As in the case of the parachor, molar refractions of many substances can be calculated from atomic and structural values, a list of which are given in Appendix D. For toluene the calculated value is:

$$7 \times 2.418 + 8 \times 1.10 + 3 \times 1.733 + 0 = 30.92$$

The value from equation (3) is 31.06.

It seemed possible that, like the parachor and molar refraction, the critical constants themselves may be computed with greater accuracy than at present by a method similar to that used in these two cases. That is, that in each of the three cases of critical volume, critical temperature and critical pressure, there may exist a series of values, one for each atom and structural element, from which, by simple addition, the critical constants may be computed for any substance. It is the object here to explore this possibility.

PROCEDURE

III PROCEDURE

(1) CRITICAL VOLUMES

The proposal is that the Critical Volume of a compound expressed in ccs./grm. mol may be represented by the relationship:

$$V_c = \sum p \quad X \quad , \tag{4}$$

where X is an elemental volume having a particular value for each atom and structural element.
p is the number of atoms or structural elements corresponding to X in the molecule.

If this proposal is correct, then the molal critical volumes of the paraffin hydrocarbons, chemical formula $C_n H_{2n+2}$, may be represented as follows:

$$V_c = n\,C + (2n + 2)H$$

$$= n(C + 2H) + 2H \tag{5}$$

Here C is the value assigned to the carbon atom and H that assigned to the hydrogen atom..

It is seen from equation (5) that if for this series the molal critical volume for each member is plotted against the corresponding number of carbon atoms, a straight line should result, the intercept of this line on the V_c - axis at n = 0 giving the numerical value of 2H and the slope of the line the numerical value of (C + 2H) from which both C and H may be evaluated.

Such a plot is presented on Figure 1 indicating the linear relationship and confirming in the case of the

paraffin hydrocarbons the validity of the proposal.

Extending the argument to the case of alcohols and ethers, it is seen that the molal critical volumes of these compounds may be represented:

$$V_c = n(C + 2H) + 2H + O \qquad (6)$$

- since a molecule contains n carbon atoms, (2n + 2) hydrogen atoms and one oxygen atom. O is the value assigned to the oxygen atom. Thus, to meet the conditions of the proposal, a plot of V_c versus n for these compounds must produce a straight line of slope equal to that in the paraffin hydrocarbon case.

Making the necessary plot (Figure 2), it was found that this condition, too, is met by the experimental data. The intercept value of V_c at $n = 0$ was thus obtained and since this is equal to (2H + O), O was evaluated.

In the case of the esters and carboxylic acids, a molecule contains n carbon atoms, 2n hydrogen atoms, two oxygen atoms and one double bond between a carbon and an oxygen atom. Hence, it may be expected that:

$$V_c = n(C + 2H) + 2 \times O + D_{CO} \qquad (7)$$

Again a straight line of the same slope as in the previous cases resulted from a plot of V_c against n (Figure 3) for these compounds and hence D_{CO}, the value for the carbon-oxygen double bond, was evaluated.

Chlorine-substituted paraffins were used to obtain the elemental value for chlorine. Methane may have either one, two, three, or four of its hydrogen atoms substituted by chlorine atoms and if m represents the number of such substitutions, then these compounds contain one carbon atom, m chlorine atoms and (4 - m) hydrogen atoms. Thus:

$$V_c = C + (4 - m)H + m\,Cl$$
$$= m(Cl - H) + C + 4H \qquad (8)$$

The slope of the straight line obtained by plotting V_c against m (Figure 4) gave (Cl - H) and hence Cl. Its intersection on the V_c - axis at m = 0, which is (C + 4H), was found to be in close agreement with the critical volume of methane.

Furthermore, paraffins with one hydrogen atom substituted by one chlorine atom contain n carbon atoms, (2n + 1) hydrogen atoms and one chlorine atom and hence:

$$V_c = n\,C + (2n + 1)\,H + Cl$$
$$= n(C + 2H) + H + Cl \qquad (9)$$

A plot of V_c versus n for these compounds was made (Figure 5) and produced a straight line the slope of which was in agreement with previous cases and the value obtained for Cl was in agreement with that evaluated from equation (8).

Amines contain n carbon atoms, (2n + 3) hydrogen atoms, and one nitrogen atom and therefore:

$$V_c = n\,C + (2n + 3)\,H + N$$
$$= n(C + 2H) + 3H + N \qquad (10)$$

Unfortunately, values of the critical volume are reported for only two amines and though these can be plotted similarly to other series, the value for N was obtained by calculating it in each of the two cases from equation (10) and by taking the mean of these two calculated values.

Nitriles contain a carbon-nitrogen triple bond. The critical volumes of these compounds by reasoning similar to that above may be represented:

$$V_c = n(C + 2H) + N - H + T_{cn} \qquad (11)$$

A plot (Figure 6) of V_c versus n, the number of carbon atoms, yielded a straight line of slope consistent with previous plots and an intercept from which T_{cn}, the value to be assigned to the carbon-nitrogen triple bond was evaluated.

A review of reported experimental critical volumes shows that in no further cases are there sufficient numbers of any series containing a yet unknown elemental value to enable plots to be made similar to those described above. The technique adopted for further evaluations was similar to that used in obtaining a value for nitrogen from the amines.

Thus from the reported olefins and diolefins, a value for the carbon-carbon double bond, D_{cc}, was obtained; and thence from the known critical volumes of the aromatics, a value for the six-membered ring, R_6, was determined.

The experimentally determined critical volumes of mercaptans and organic sulfides were used to obtain a value, S, for sulfur. Further to this sufficient compounds containing the remaining halogens are available and these were used to obtain values for F, Br and I. Though the critical volume of only one compound with a carbon to carbon triple bond, namely acetylene, is reported, it was considered desirable to evaluate T_{cc} from this single result. Again, since the value of the carbon to oxygen double bond gave good predictions for carbon disulfide and sulfur dioxide, it was decided that this value be assigned to the carbon to sulfur and sulfur to oxygen double bonds also.

In all the cases outlined above where, for an element, values had to be calculated separately from several different compounds and averaged to give a mean, very good agreement was obtained between these calculated values.

The elements for which elemental critical volumes have been determined make it possible to calculate the molal critical volume for the majority of compounds met with in industry. There are reported critical volumes which make it possible to calculate a few more elemental values from single cases but this was not done since no check on such calculated values was possible. Further experimental data is required so that for any given element, a value may be calculated from at least two different compounds in order to provide the necessary check.

(2) CRITICAL TEMPERATURES

The ratio of the normal boiling temperature, T_b, to the critical temperature, T_c, both expressed in degrees Kelvin, was found to obey a rule similar to that described for critical volumes. The ratio T_b/T_c may be represented by the relationship:

$$T_b/T_c = \sum q \quad Y \tag{12}$$

where Y is a number having a particular value for each atom and structural element.
q is the number of atoms or structural elements corresponding to Y in the molecule.

For the paraffin hydrocarbons, therefore,

$$T_b/T_c = n\,C + (2n + 2)H$$

$$= n(C + 2H) + 2H \tag{13}$$

Again, in this case, C is used to denote the value for carbon and H that for hydrogen. A plot of T_b/T_c versus n, the number of carbon atoms in the molecule, was made and is presented on Figure 7. To obtain the best possible line through the experimental points, the method of least squares, described in Appendix E, was used. This yielded values of C and H.

As in the case of critical volumes, the different homologous series of compounds were treated successively such that each contained one unknown elemental value over those previously evaluated. In this manner the values to be assigned to each element were obtained. The order of

treatment and the T_b/T_c versus n relationships were as follows:

Olefins:

$$T_b/T_c = n(C + 2H) + D_{cc} \qquad (14)$$

- from which the carbon-carbon double bond value, D_{cc}, was obtained (see Figure 8).

Aromatics:

$$T_b/T_c = n(C + 2H) + R_6 + 3\ D_{cc} - 6H \qquad (15)$$

- from which R_6, the six-membered ring, was evaluated (see Figure 8).

Ethers:

$$T_b/T_c = n(C + 2H) + 2H + O \qquad (16)$$

- which yielded O, the oxygen value (Figure 9).

Esters:

$$T_b/T_c = n(C + 2H) + 2 \times O + D_{co} \qquad (17)$$

- gave the value for the carbon-oxygen double bond (Figure 10).

Carboxylic Acids:

Though these compounds are isomeric with the esters, it was discovered that the plot of T_b/T_c versus n (Figure 11) gave a straight line parallel to that given by the plot for the esters. The difference, structurally, is that the carboxylic acids contain a hydroxyl group and by assuming that the value for this is different than that given by the

addition of the oxygen and hydrogen values, this difference was explained. Thus, for the carboxylic acids:

$$T_b/T_c = n(C + 2H) + O + D_{co} - H + (OH) \qquad (18)$$

- which gave the postulated (OH) value.

Alcohols:

In the case of these compounds, the only serious discrepancy from a straight line of slope (C + 2H) as obtained from the paraffin hydrocarbon plot was found. To overcome the difficulty the (OH) value determined from the carboxylic acids was used and this gave a line through the experimental points which could not be improved upon. For the alcohols:

$$T_b/T_c = n(C + 2H) + H + (OH) \qquad (19)$$

Amines:

$$T_b/T_c = n(C + 2H) + 3H + N \qquad (20)$$

The plot of the experimental points in this case (Figure 11) gave the value for N.

Nitriles:

$$T_b/T_c = n(C + 2H) + N - H + T_{cn} \qquad (21)$$

- from which T_{cn}, the carbon-nitrogen triple bond value was obtained, the plot being presented on Figure 12.

Sulfides and Mercaptans:

The organic mono-sulfides and mercaptans are isomeric with each other and a combined plot of T_b/T_c versus n for both series of compounds (Figure 12) yielded a single straight line from which the sulfur value, S, was obtained.

$$T_b/T_c = n(C + 2H) + 2H + S \quad (22)$$

Acetylenes:

$$T_b/T_c = n(C + 2H) - 2H + T_{cc} \quad (23)$$

A plot of T_b/T_c versus n in this case (Figure 13) gave the value for T_{cc}, the carbon-carbon triple bond.

Lack of data made it impossible to determine further elemental values by the plotting technique, but values for the halogen elements were determined by a method analogous to that described for critical volumes, namely, the value was calculated for each compound containing the desired element for which critical temperature data exists. A mean of these values, which were found to be in close agreement, was taken. As with critical volumes, the value found for the carbon to oxygen double bond yielded good predictions for carbon disulfide and sulfur dioxide and so this value was assigned to the carbon to sulfur and sulfur to oxygen double bonds also.

(3) CRITICAL PRESSURES

Meissner and Redding (44) found that critical pressures may be computed with reasonable accuracy from the relationship:

$$P_c = 20.8\ T_c/(V_c - 8) \qquad (24)$$

Both this and the proposal by Wohl (68) and (69):

$$P_c = 21.8\ T_c/V_c \qquad (25)$$

- may be expressed in the form:

$$T_c/P_c = A\ V_c + B \qquad (26)$$

where A and B are constants. Remembering that:

$$V_c = C\ n + D \qquad (27)$$

where C and D are constants, characteristic of each homologous series and predictable from atomic and structural values.
and n is the number of carbon atoms in the molecule considered.

- it may be expected that:

$$T_c/P_c = A'\ n + B' \qquad (28)$$

where A' and B' are constants of a similar nature to those of equation (26).

Plotting the ratio of T_c/P_c versus n for a number of homologous series produces a series of curves which have slightly varying slopes and which have a definite curvature.

A study of these curves led to the suggestion that a relationship of the form:

$$T_c/P_c^{\,a} = A'\ n + B' \qquad (29)$$

may give the desired results, "a" being a constant such

that: $0 < a < 1.0$, the other terms having the same significance as before. This is equivalent to saying:

$$T_c/P_c^{\,a} = \sum r\,Z \qquad (30)$$

where Z is a number having a particular value for each atom and structural element.
r is the number of atoms or structural elements corresponding to Z in the molecule.

A study of this proposal was made and it was found that in the cases of the paraffin hydrocarbons, olefins, aromatics, ethers, esters, amines, chlorine-substituted paraffins, sulfides and mercaptans, a value of "a" equal to 0.80 gave plots of $T_c/P_c^{\,a}$ versus n which were straight lines of equal slope. These plots are presented on Figures 14 to 18. From them, elemental values of C, H, D_{cc}, R_6, O, D_{co}, N, Cl and S were obtained by a method analogous to that used for critical volumes and critical temperatures.

Using the exponent of 0.80 for the alcohols, nitriles, carboxylic acids and phenols gave plots neither parallel to those already considered nor straight. However, it was found that by assigning different values for the exponent for each series the plots of $T_c/P_c^{\,a}$ versus n could be made straight and parallel to those above. It was found that the exponents to be used were:

0.65 for the alcohols

0.68 for the nitriles

0.685 for the carboxylic acids and

0.665 for the phenols.

Plots of T_c/P_c^a versus n for the first two of these cases are presented on Figures 19 and 20 and from them values for the (OH) group and the carbon to nitrogen triple bond were obtained.

Values for F, Br, I, T_{cc} and T_{nn} were calculated from the experimental data for isolated compounds, average values being taken in each case. The carbon to sulfur double bond value was assumed to be equal to those for the carbon to carbon and the carbon to oxygen double bonds since this gave a reasonable prediction for carbon disulfide using an exponent of 0.80. Similarly the sulfur to oxygen double bond was assumed to be equal to this value since it gave a prediction not greatly in error for sulfur dioxide.

RESULTS

IV RESULTS

(1) CRITICAL VOLUMES

Experimental and calculated data are presented in tabular and graphical form. The first two columns of the tables contain the experimental values of the Critical Volume and the corresponding number of carbon atoms in the molecule respectively. From these two columns, the graphs have been plotted. The values assigned to the different elements have in turn been determined from these graphs. The third column contains the Critical Volumes as calculated from these elemental values. Finally, the deviations of the calculated from the experimental values are presented together with these deviations expressed as percentages of the experimentally determined values.

TABLE II

Critical Volumes of Paraffin Hydrocarbons

Compound	Exp'l V_c	nn	Calc'd V_c	Dev'n	% Dev'n
Methane	97.8	1	91.0	- 6.8	- 6.9
Ethane	142.9	2	148.0	+ 5.1	+ 3.6
Propane	194.7	3	205.0	+10.3	+ 5.3
Butane	266.6	4	262.0	- 4.6	- 1.7
Pentane	318.9	5	319.0	+ 0.1	0.0
Hexane	366.9	6	376.0	+ 9.0	+ 2.5
Heptane	427.2	7	433.0	+ 5.8	+ 1.4
Octane	489.9	8	490.0	+ 0.1	0.0

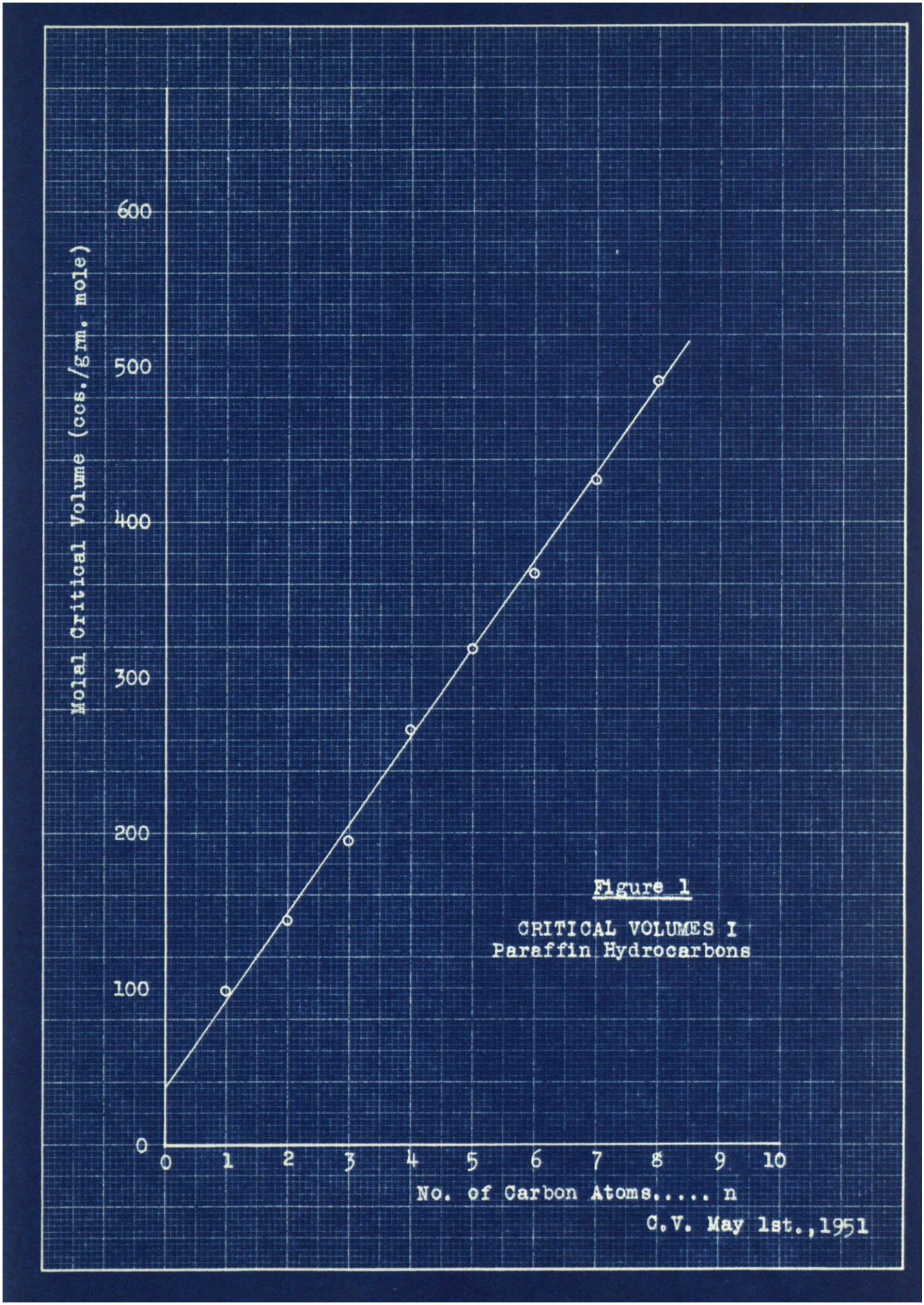

Figure 1

CRITICAL VOLUMES I
Paraffin Hydrocarbons

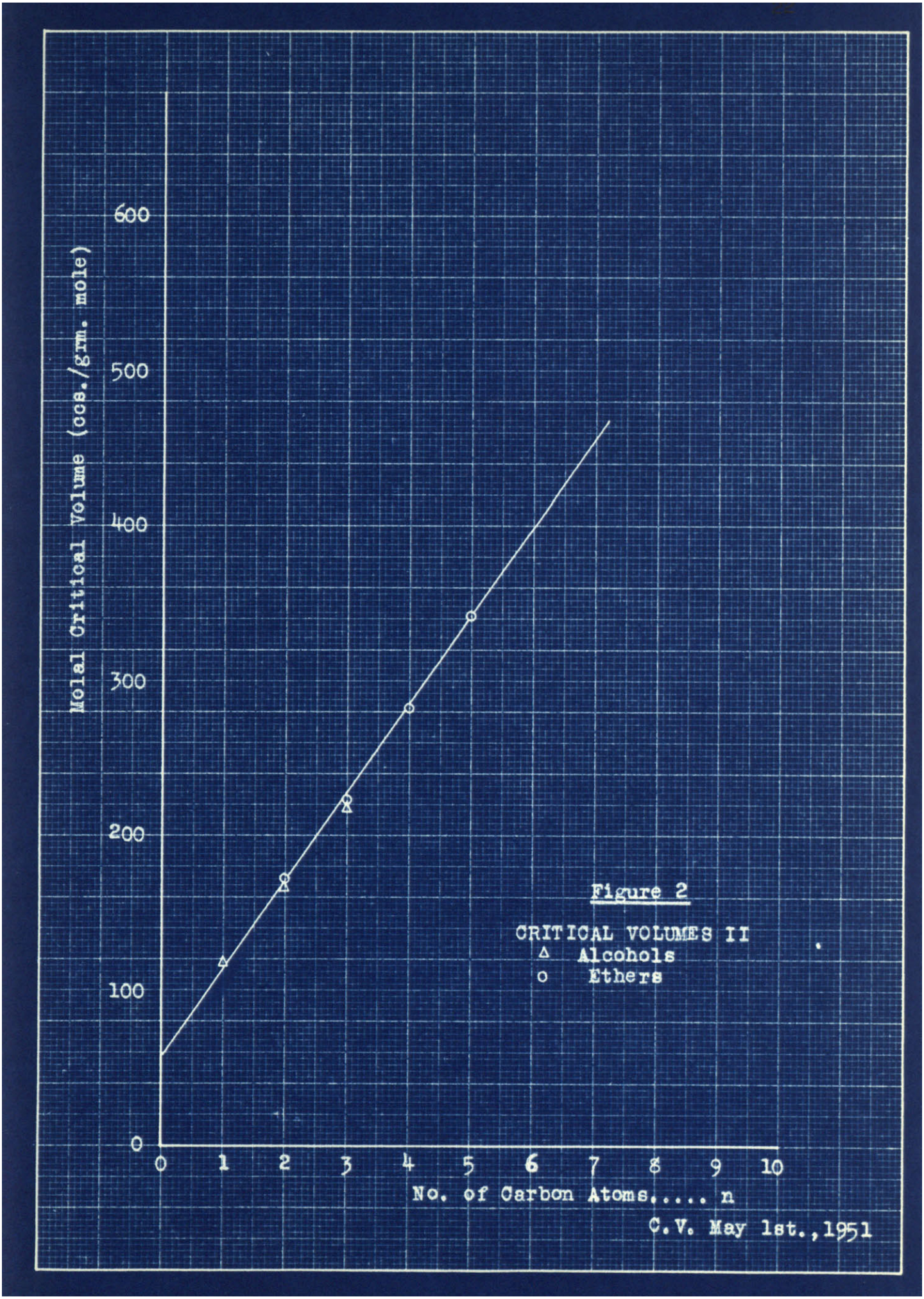

Figure 2

CRITICAL VOLUMES II
△ Alcohols
o Ethers

Experimental values of V_c versus n for the Paraffin Hydrocarbons are plotted on Figure 1 from which:

Slope of Curve = C + 2H = 57.0) Hence C = 23.0

V_c at n = 0 = 2H = 34.0) H = 17.0

TABLE III

Critical Volumes of Alcohols and Ethers

Compound	Exp'l V_c	n	Calc'd V_c	Dev'n	% Dev'n
Methyl Alcohol	117.7	1	112.0	- 5.7	- 4.8
Ethyl Alcohol	167.3	2	169.0	+ 1.7	+ 1.0
n-Propyl Alcohol	219.8	3	226.0	+ 6.2	+ 2.8
Methyl Ether	169.7	2	169.0	- 0.7	- 0.4
Methyl Ethyl Ether	222.2	3	226.0	+ 3.8	+ 1.7
Ethyl Ether	282.4	4	283.0	+ 0.6	+ 0.2
Ethyl Propyl Ether	341.1	5	340.0	- 1.1	- 0.3

Experimental values of V_c versus n for the Alcohols and Ethers are presented on Figure 2 from which:

V_c at n = 0 = 2H + O = 55.0, Hence O= 21.0

TABLE IV(a)

Critical Volumes of Carboxylic Acids

Compound	Exp'l V_c	n	Calc'd V_c	Dev'n	% Dev'n
Acetic	170.9	2	174.0	+ 3.1	+ 1.8
Propionic Acid	234.9	3	231.0	- 3.9	- 1.7
n-Butyric Acid	291.4	4	288.0	- 3.4	- 1.2
i-Butyric Acid	290.0	4	288.0	- 2.0	- 0.7

TABLE IV(b)

Critical Volumes of Esters

Compound	Exp'l V_c	n	Calc'd V_c	Dev'n	% Dev'n
Methyl Formate	171.9	2	174.0	+ 2.1	+ 1.2
Ethyl Formate	229.1	3	231.0	+ 1.9	+ 0.8
Propyl Formate	284.8	4	288.0	+ 3.2	+ 1.1
Isobutyl Formate	354.2	5	345.0	- 9.2	- 2.6
Isoamyl Formate	411.4	6	402.0	- 9.4	- 2.3
Methyl Acetate	227.7	3	231.0	+ 3.3	+ 1.5
Ethyl Acetate	285.7	4	288.0	+ 2.3	+ 0.8
Propyl Acetate	344.6	5	345.0	+ 0.4	+ 0.1
Isobutyl Acetate	415.8	6	402.0	-13.8	- 3.3
Methyl Propionate	282.1	4	288.0	+ 5.9	+ 2.1
Ethyl Propionate	344.6	5	345.0	+ 0.4	+ 0.1
Methyl Butyrate	340.0	5	345.0	+ 5.0	+ 1.5
Methyl Isobutyrate	339.0	5	345.0	+ 6.0	+ 1.8
Ethyl Butyrate	405.8	6	402.0	- 3.8	- 0.9
Ethyl Isobutyrate	420.0	6	402.0	-18.0	- 4.3
Methyl Valerate	415.8	6	402.0	-13.8	- 3.3

Experimental values of V_c versus n for the Carboxylic Acids and the Esters are presented on Figure 3 from which:

V_c at n = 0 $= D_{CO} + 2 \times 0 = 60.0$

Hence $\underline{D_{CO} = 18.0}$

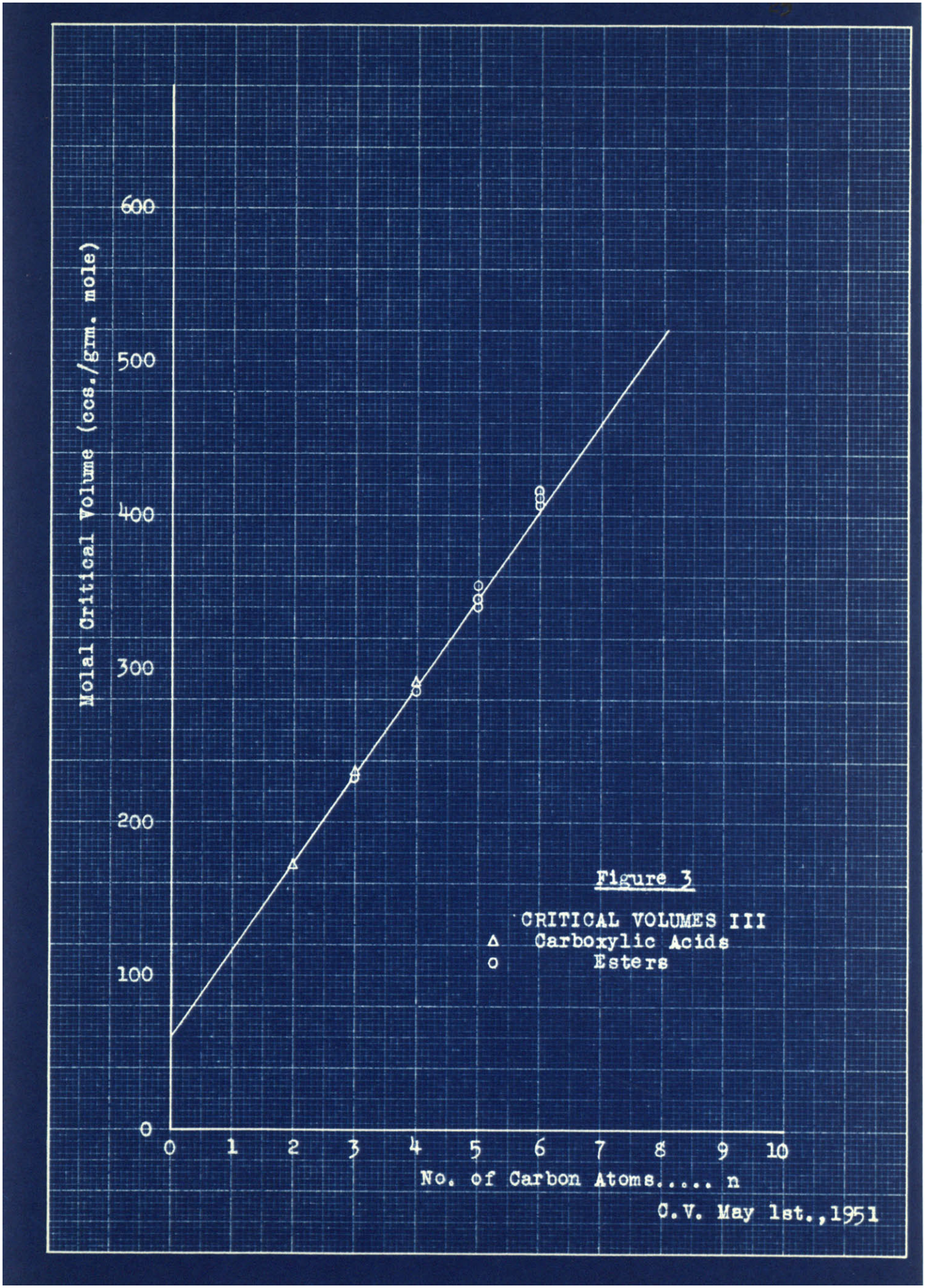
Molal Critical Volume (ccs./grm. mole)
600
500
400
300
200
100
0
0 1 2 3 4 5 6 7 8 9 10
No. of Carbon Atoms..... n
Figure 3
CRITICAL VOLUMES III
Δ Carboxylic Acids
o Esters
C.V. May 1st., 1951

TABLE V

Critical Volumes of Chlorine-substituted Methanes

Compound	Exp'l V_c	m	Calc'd V_c	Dev'n	% Dev'n
Methyl Chloride	136.5	1	137.5	+ 1.0	+ 0.7
Chloroform	231.0	3	230.5	- 0.5	- 0.2
Carbon Tetrachloride	276.0	4	277.0	+ 1.0	+ 0.4

Experimental values of V_c versus m for the Chlorine-substituted Methanes are presented on Figure 4 from which:

Slope of Curve = Cl - H = 46.5 Hence Cl = 63.5

TABLE VI

Critical Volumes of Chlorine-substituted Paraffins

Compound	Exp'l V_c	n	Calc'd V_c	Dev'n	% Dev'n
Methyl Chloride	136.5	1	137.5	+ 1.0	+ 0.7
Ethyl Chloride	195.5	2	194.5	- 1.0	- 0.5

Experimental values of V_c versus n for the Chlorine-substituted Paraffins are presented on Figure 5 from which:

V_c at n = 0 = H + Cl = 80.5 Hence Cl = 63.5

- thus confirming the value obtained from Figure 4.

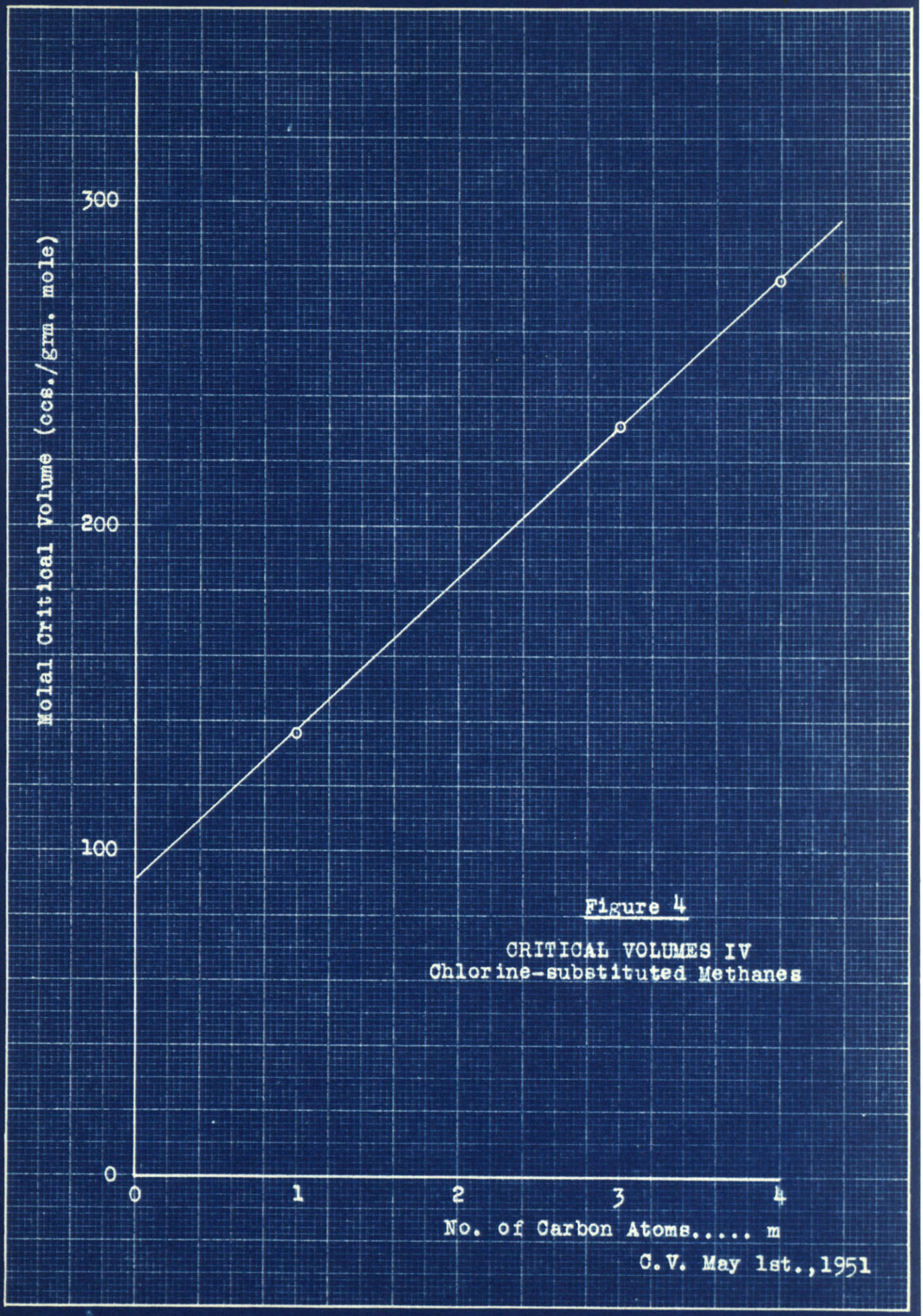

Figure 4

CRITICAL VOLUMES IV
Chlorine-substituted Methanes

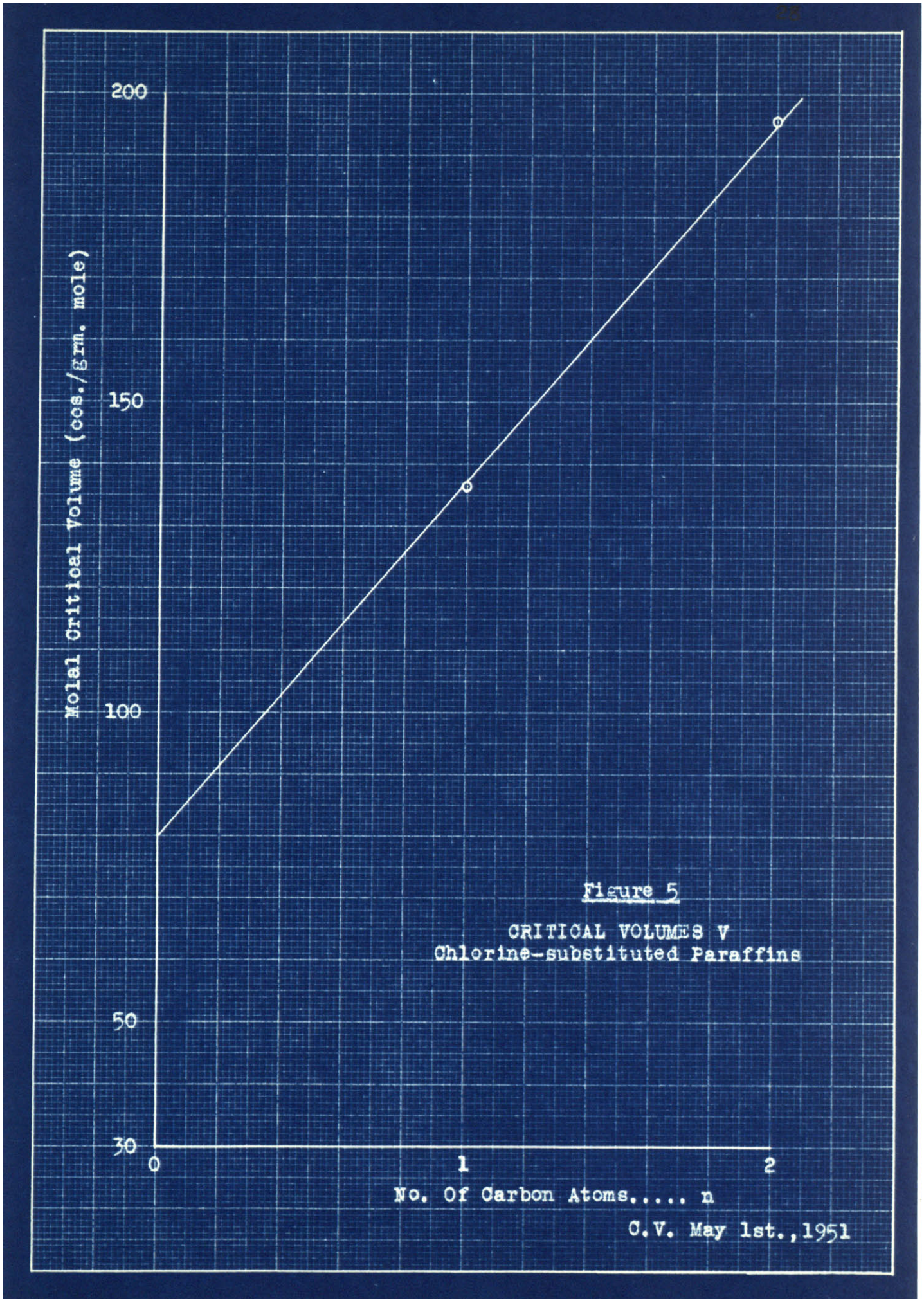

Figure 5

CRITICAL VOLUMES V
Chlorine-substituted Paraffins

C.V. May 1st., 1951

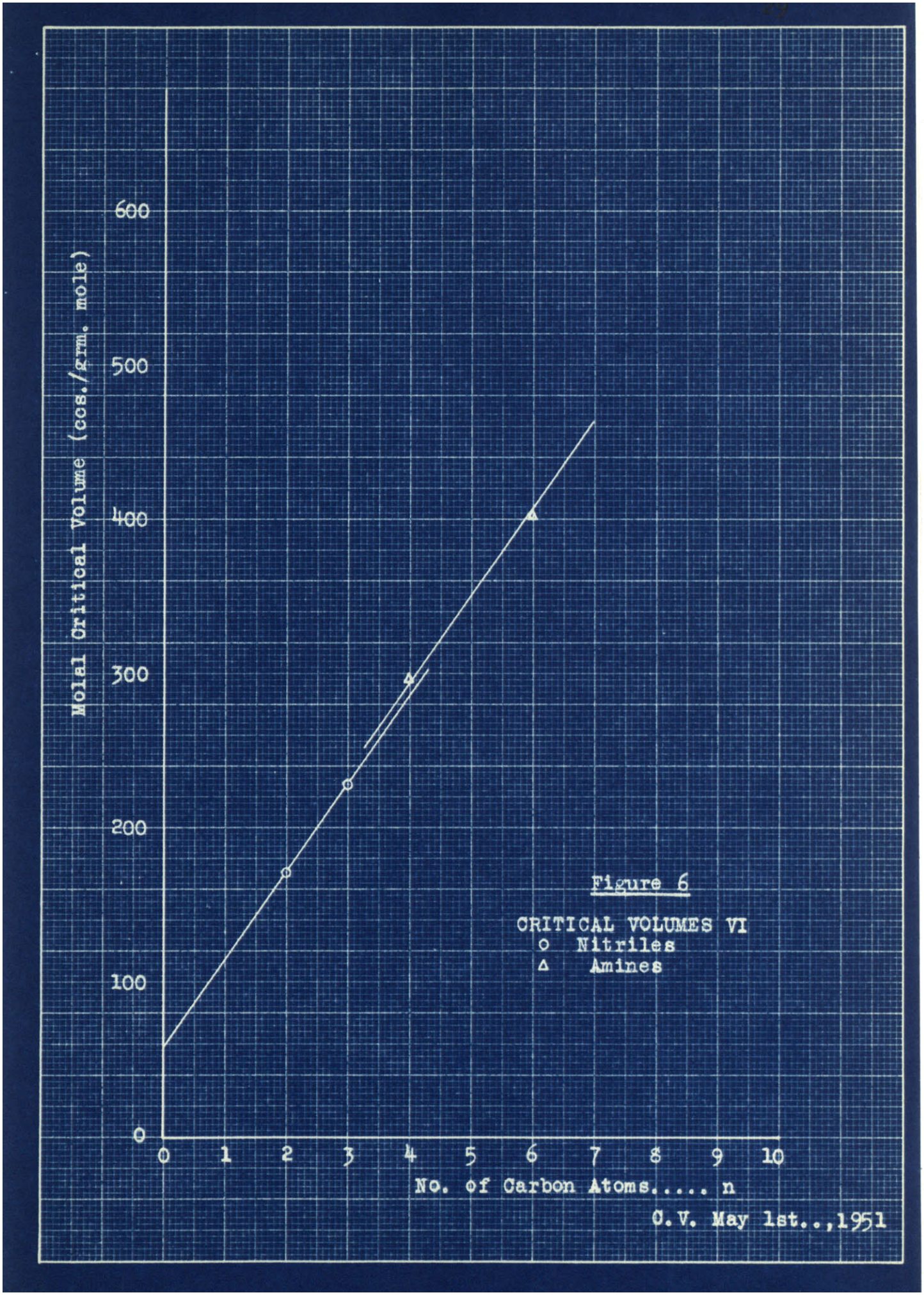
Molal Critical Volume (cos./grm. mole)
600
500
400
300
200
100
0
0 1 2 3 4 5 6 7 8 9 10
No. of Carbon Atoms..... n
Figure 6
CRITICAL VOLUMES VI
o Nitriles
Δ Amines
O.V. May 1st..,1951

TABLE VII

Critical Volumes of Nitriles

Compound	Exp'l V_c	n	Calc'd V_c	Dev'n	% Dev'n
Acetonitrile	171.0	2	171.0	0.0	0.0
Propionitrile	228.5	3	228.0	- 0.5	- 0.2

Experimental values of V_c versus n for the Nitriles are presented on Figure 6 from which:

V_c at n = 0 $= N + T_{cn} - H = 57.0$

Hence $N + T_{cn} = 74.0$

Amines

Diethylamine: Experimental $V_c = 297.0$

$N = 297 - 4xC - 11xH = 297 - 92 - 187 = 18.0$

Triethylamine: Experimental $V_c = 402.0$

$N = 402 - 6xC - 15xH = 402 - 138 - 255 = 9.0$

Mean Value of $N = 13.5$

Hence $T_{cn} = 60.5$

Sulfides and Mercaptans

Methyl Sulfide: Experimental $V_c = 203.0$

$S = 203 - 2xC - 6xH = 203 - 46 - 102 = 55.0$

Ethyl Sulfide: Experimental $V_c = 323.0$

$S = 323 - 4xC - 10xH = 323 - 92 - 170 = 61.0$

Methyl Mercaptan: Experimental $V_c = 148.8$

$S = 148.8 - C - 4xH = 148.8 - 23 - 68 = 57.8$

Ethyl Mercaptan: Experimental $V_c = 206.0$

$S = 206 - 2xC - 6xH = 206 - 46 - 102 = 58.0$

Mean Value of $S = 58.0$

Olefins and Diolefins

Ethylene: Experimental $V_c = 127.2$

$$D_{cc} = 127.2 - 2xC - 4xH = 127.2 - 46 - 68 = 13.2$$

Butadiene-1,3: Experimental $V_c = 220.5$

$$2xD_{cc} = 220.5 - 4xC - 6xH = 220.5 - 92 - 102 = 26.5$$

Mean Value of $D_{cc} = 13.2$

Aromatics

Benzene: Experimental $V_c = 256.2$

$$R_6 = 256.2 - 6xC - 6xH - 3xD_{cc}$$
$$= 256.2 - 138 - 102 - 39.6 = -23.4$$

Toluene: Experimental $V_c = 315.1$

$$R_6 = 315.1 - 7xC - 8xH - 3xD_{cc}$$
$$= 315.1 - 161 - 136 - 39.6 = -21.5$$

Mean Value of $R_6 = -22.5$

Acetylenes

Acetylene: Experimental $V_c = 112.7$

$$T_{cc} = 112.7 - 2C - 2H$$
$$= 112.7 - 46 - 34 = 32.7$$

Mean Value of $T_{cc} = 32.7$

Fluorine-substituted Hydrocarbons

Dichlorodifluoromethane: Experimental $V_c = 218.0$

$$2xF = 218 - C - 2xCl = 218 - 23 - 137 = 68.0$$

Fluorobenzene: Experimental $V_c = 271.5$

$$F = 271.5 - 6xC - 5xH - R_6 - 3xD_{cc}$$
$$= 271.5 - 138 - 85 + 22.5 - 39.6 = 31.4$$

Mean Value of $F = 33.1$

Bromine-substituted Hydrocarbons

Ethyl Bromide: Experimental $V_c = 212.3$

$$Br = 212.3 - 2xC - 5xH = 212.3 - 46 - 85 = 81.3$$

Bromobenzene: Experimental $V_c = 322.8$

$$Br = 322.8 - 6xC - 5xH - R_6 - 3xD_{cc}$$
$$= 322.8 - 138 - 85 + 22.5 - 39.6 = 82.7$$

Mean Value of Br = 82.0

Iodine-substituted Hydrocarbons

The experimental value for only one of these compounds, iodobenzene, is reported, but such excellent agreement is found for the other halogens that it was considered worth while to calculate the value of I from this.

Iodobenzene: Experimental $V_c = 351.0$

$$I = 351.0 - 6xC - 5xH - R_6 - 3xD_{cc}$$
$$= 351.0 - 138 - 85 + 22.5 - 39.6 = 110.9$$

Hence I = 110.9

TABLE VIII

Comparison of Experimental and Calculated Values of Critical Volume for Amines, Sulfides, Mercaptans, Olefins, Diolefins, Aromatics, Halogen-substituted and remaining Hydrocarbons.

Compound	Exp'l V_c	Cal'd V_c	Dev'n	% Dev'n
Diethylamine	297.0	292.5	- 4.5	- 1.5
Triethylamine	402.0	406.5	+ 4.5	+ 1.1
Methyl Mercaptan	148.8	149.0	- 0.2	- 0.1
Ethyl Mercaptan	206.0	206.0	0.0	0.0
Methyl Sulfide	203.0	206.0	+ 3.0	+ 1.5

TABLE VIII (cont)

Compound	Exp'l V_c	Cal'd V_c	Dev'n	% Dev'n
Ethyl Sulfide	323.0	320.0	- 3.0	- 0.9
Ethylene	127.2	127.2	0.0	0.0
Butadiene-1,3	220.5	220.4	- 0.1	0.0
Benzene	256.2	257.1	+ 0.9	+ 0.4
Toluene	315.1	314.1	- 1.0	- 0.3
Dichlorodifluoromethane	218.0	215.7	- 2.3	- 1.1
Fluorobenzene	271.5	273.6	+ 2.1	+ 0.8
Chlorobenzene	308.2	303.6	- 4.6	- 1.5
Ethyl Bromide	212.3	213.0	+ 0.7	+ 0.3
Bromobenzene	322.8	322.1	- 0.7	- 0.2
Iodobenzene	351.1	351.1	0.0	0.0
Cyclohexane	308.0	319.5	+11.5	+ 3.7
Biphenyl	448.9	480.2	+31.3	+ 7.0
2-Methylbutane	308.0	319.0	+11.0	+ 3.6
2,3-Dimethylbutane	357.0	376.0	+19.0	+ 5.3
2,5-Dimethylhexane	428.0	490.0	+ 8.0	+ 1.7
2,2,3,3-Trimethylhexane	428.0	490.0	+ 8.0	+ 1.7

TABLE IX

Critical Volumes of Inorganic Compounds

Compound	Exp'l V_c	Cal'd V_c	Dev'n	% Dev'n
Ammonia	72.4	65.0	- 7.4	-10.2
Carbon Dioxide	95.7	101.0	+ 5.3	+ 5.5
Carbon Disulfide	172.5	175.0	+ 2.5	+ 1.4

TABLE IX (cont)

Compounds	Exp'l V_c	Cal'd V_c	Dev'n	% Dev'n
Chlorine	124.0	127.0	+ 3.0	+ 2.4
Hydrogen	64.5	34.0	-30.5	-47.3
Hydrogen Chloride	87.0	80.5	- 6.5	- 7.5
Hydrogen Cyanide	135.0	114.0	-21.0	-15.5
Nitrogen	90.0	87.5	- 2.5	- 2.8
Oxygen	74.5	60.0	-14.5	-19.5
Water	54.1	55.0	+ 0.9	+ 1.7
Water Vapor	45.0	55.0	+10.0	+18.2
Sulfur Dioxide	123.2	118.0	- 5.2	- 4.2
Sulfur Trioxide	127.0	139.0	+12.0	+ 9.4

TABLE X

List of Atomic and Structural Values -- Critical Volumes

Atomic or Structural Element	Symbol	Value
Carbon	C	23.0
Hydrogen	H	17.0
Oxygen	O	21.0
Nitrogen	N	13.5
Sulfur	S	58.0
Fluorine	F	33.1
Chlorine	Cl	63.5
Bromine	Br	82.0
Iodine	I	110.9

TABLE X (cont)

Atomic or Structural Element	Symbol	Value
Double Bond (C=C)	D_{cc}	13.2
Double Bond (C=O)	D_{co}	18.0
Double Bond (C=S)	D_{cs}	18.0
Double Bond (S=O)	D_{so}	18.0
Triple Bond (C≡C)	T_{cc}	32.7
Triple Bond (C≡N)	T_{cn}	60.5
Triple Bond (N≡N)	T_{nn}	60.5
Six-membered Ring (Aromatic & Naphthenic)	R_6	-22.5

(2) CRITICAL TEMPERATURES

Experimental and calculated data are again presented in both tabular and graphical form in a manner similar to that used for Critical Volumes.

The first two columns of the tables contain the experimentally determined Normal Boiling and Critical Temperatures, expressed in degrees Kelvin. Following these are the ratios of the Normal Boiling to the Critical Temperatures and the corresponding number of carbon atoms in the molecule, n. From these two columns, the graphs of the Normal Boiling to Critical Temperature Ratio versus Number of Carbon Atoms in the molecule have been plotted. The values assigned to the various elements have been determined from these graphs. Columns (5) and (6) present the calculated values of the Normal Boiling to the Critical Temperature Ratio and the Critical Temperature respectively. Finally, the deviations of the calculated from the experimental values of the Critical Temperature are presented together with these deviations expressed as percentages of the experimentally determined values.

TABLE XI

Critical Temperatures of Paraffin Hydrocarbons

Compound	Exp'l T_b	Exp'l T_c	Exp'l T_b/T_c	n	Calc'd T_b/T_c	Calc'd T_c	Dev'n	% Dev'n
Methane	111.8	190.7	0.5863	1	0.5908	189.0	- 1.7	- 0.9
Ethane	184.9	305.3	0.6056	2	0.6066	305.0	- 0.3	- 0.1
Propane	228.7	370.2	0.6178	3	0.6224	367.5	- 2.7	- 0.7
Butane	273.8	425.2	0.6439	4	0.6382	429.0	+ 3.8	+ 0.9
Pentane	309.4	470.4	0.6577	5	0.6540	474.0	- 0.4	- 0.1
Heptane	371.6	542.7	0.6847	7	0.6856	542.0	- 0.7	- 0.1
Nonane	423.8	596.0	0.7111	9	0.7172	591.0	- 5.0	- 0.8
Decane	447.2	603.6	0.7409	10	0.7330	610.0	+ 6.4	+ 1.0

Experimental Values of T_b/T_c versus n for Paraffin Hydrocarbons are plotted in Figure 7 from which:

Slope of Curve = C + 2H = 0.0158)
T_b/T_c at n = 0 = 2H = 0.5750)

Hence C = -0.5592
H = 0.2875

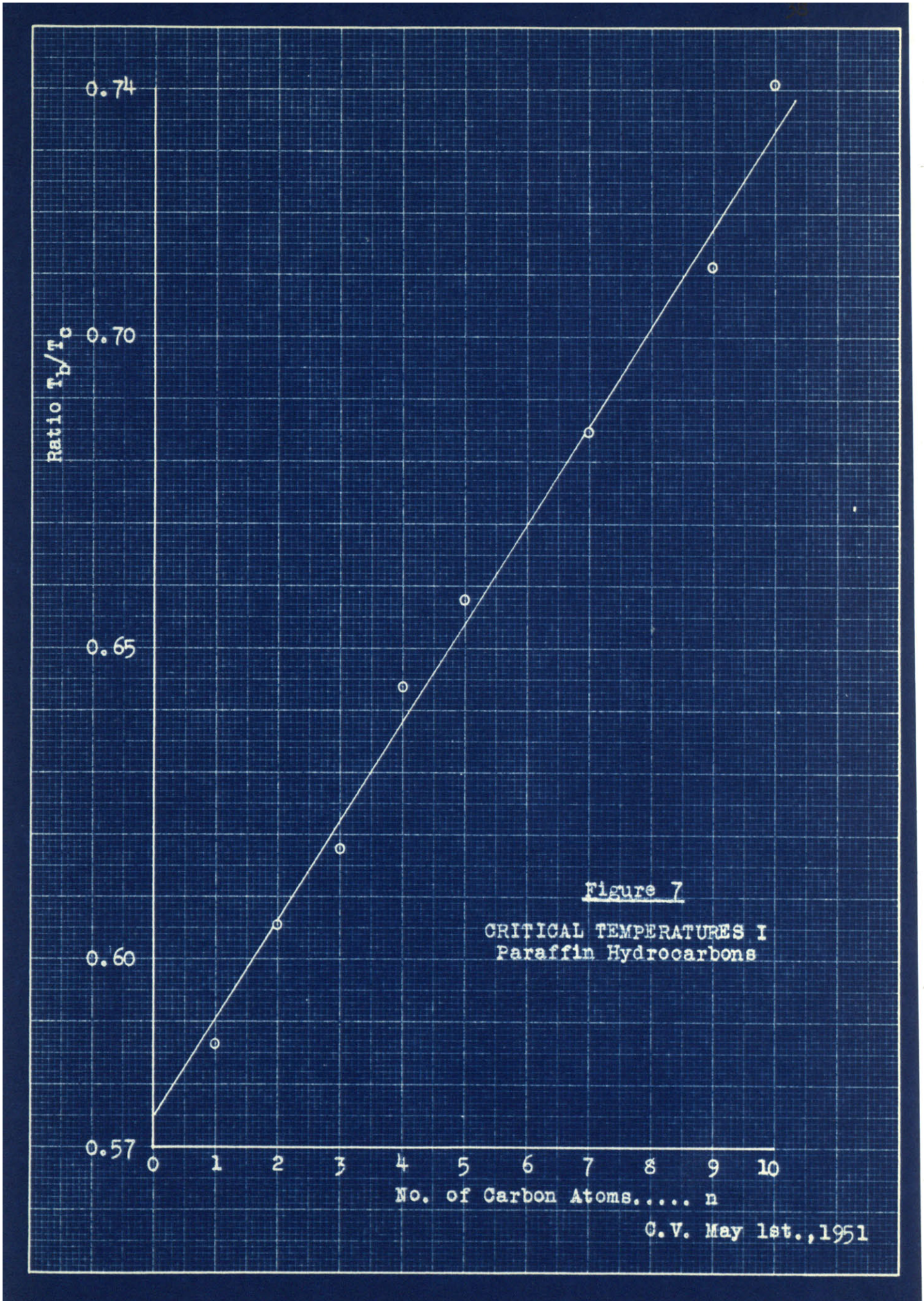

Figure 7

CRITICAL TEMPERATURES I
Paraffin Hydrocarbons

TABLE XII

Critical Temperatures of Olefins and Diolefins

Compound	Exp'l T_b	Exp'l T_c	Exp'l T_b/T_c	n	Calc'd T_b/T_c	Calc'd T_c	Dev'n	% Dev'n
Ethylene	169.4	283.1	0.5984	2	0.5956	284.5	+ 1.4	+ 0.5
Propylene	226.2	365.3	0.6192	3	0.6114	370.0	+ 4.7	+ 1.3
Butene-1	255.2	417.2	0.6117	4	0.6272	407.0	-10.2	- 2.4
Pentene-1	313.2	474.4	0.6602	5	0.6430	487.0	+12.6	+ 2.7
Hexene-1	337.3	516.7	0.6528	6	0.6588	512.0	- 4.7	- 0.9
Octene-1	396.2	578.0	0.6855	8	0.6904	575.0	- 3.0	- 0.5
Propadiene	241.2	393.9	-	-	0.6004	402.0	+ 8.1	+ 2.1
Butadiene-1,3	270.6	425.2	-	-	0.6162	439.0	+13.8	+ 3.2
Hexadiene-1,5	333.2	507.6	-	-	0.6478	514.0	+ 6.4	+ 1.3

Experimental Values of T_b/T_c versus n for the Olefins are plotted on Figure 8 from which:

$$T_b/T_c \text{ at } n = 0 \quad = \underline{D_{co} = 0.5640}$$

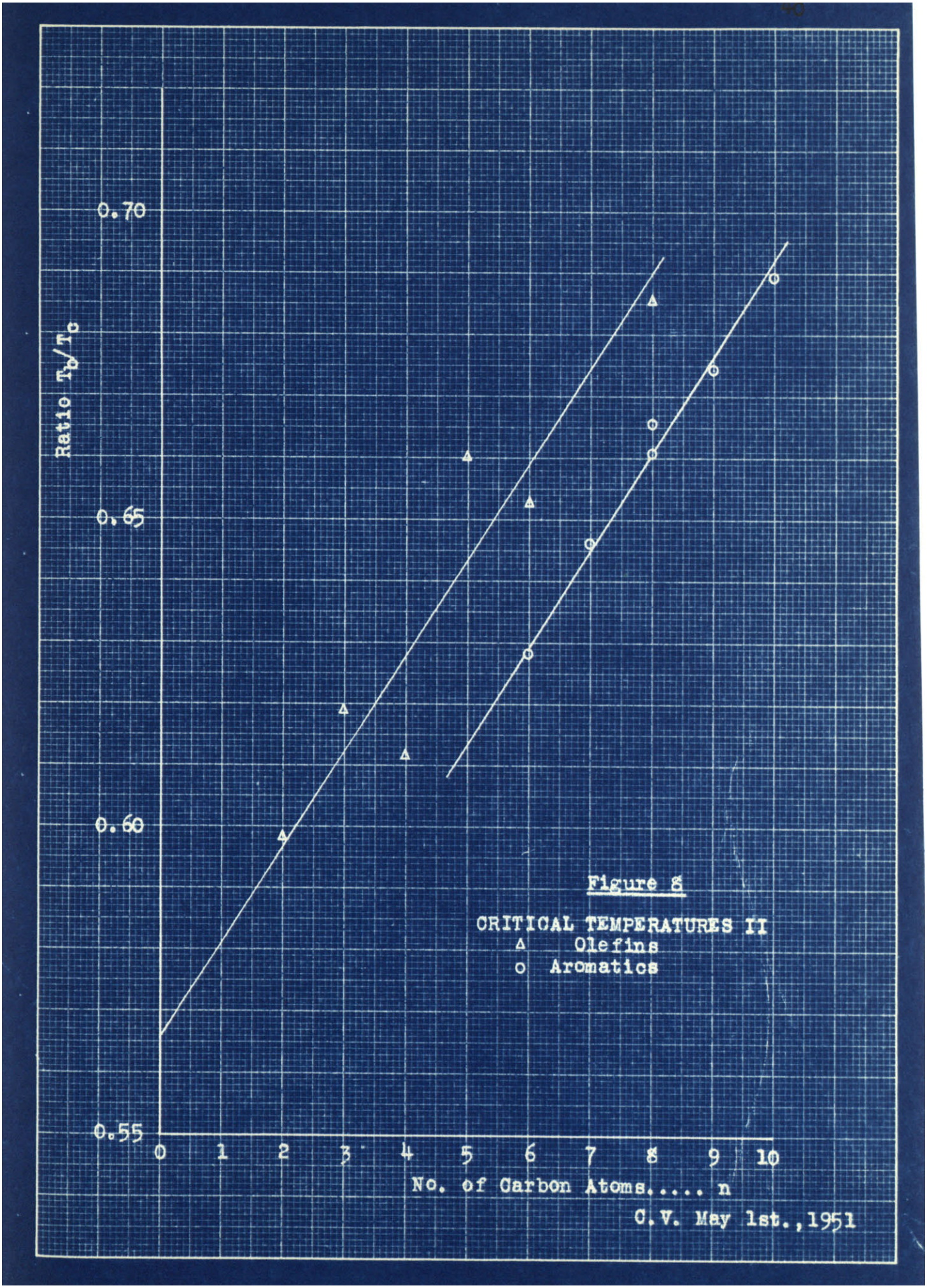

Figure 8

CRITICAL TEMPERATURES II
△ Olefins
○ Aromatics

TABLE XIII

Critical Temperatures of the Aromatics

Compound	Exp'l T_b	Exp'l T_c	Exp'l T_b/T_c	n	Calc'd T_b/T_c	Calc'd T_c	Dev'n	% Dev'n
Benzene	352.8	561.7	0.6281	6	0.6284	562.0	+ 0.3	+ 0.1
Toluene	383.7	593.8	0.6462	7	0.6442	596.0	+ 2.2	+ 0.3
o-Xylene	417.2	631.5	0.6606	8	0.6600	632.0	+ 0.5	+ 0.1
m-Xylene	412.2	618.8	0.6661	8	0.6600	625.0	+ 6.2	+ 1.0
p-Xylene	410.9	617.6	0.6653	8	0.6600	623.0	+ 5.4	+ 0.9
Ethyl Benzene	409.4	619.2	0.6612	8	0.6600	621.0	+ 1.8	+ 0.3
Propyl Benzene	430.7	638.8	0.6742	9	0.6758	637.5	- 1.3	- 0.2
Isobutyl Benzene	448.2	650.2	0.6893	10	0.6916	649.0	- 1.2	- 0.2
Pentamethyl Benzene	503.2	691.2	0.7280	11	0.7074	711.0	+19.8	+ 2.9

Experimental values of T_b/T_c versus n for the Aromatics are plotted on Figure 8 from which:

$$T_b/T_c \text{ at } n = 0 \; = 3D_{cc} + R_6 - 6H = 0.5336$$

Hence $\underline{R_6 = 0.5666}$

TABLE XIV

Critical Temperatures of the Ethers

Compounds	Exp'l T_b	Exp'l T_c	Exp'l T_b/T_c	n	Calc'd T_b/T_c	Calc'd T_c	Dev'n	% Dev'n
Methyl Ether	248.3	400.1	0.6206	2	0.6231	398.0	- 2.1	- 0.5
Methyl Ethyl Ether	281.1	437.9	0.6419	3	0.6389	440.0	+ 2.1	+ 0.5
Ethyl Ether	307.7	467.0	0.6589	4	0.6547	470.5	+ 3.5	+ 0.7
Ethyl Propyl Ether	334.6	500.6	0.6684	5	0.6705	499.0	- 1.6	- 0.3
Ethyl Allyl Ether	340.8	518.2	0.6577	-	0.6596	517.0	- 1.2	- 0.2
Methylene Diethyl Ether	362.2	527.2	0.6870	-	0.6870	527.2	0.0	0.0

Experimental values of T_b/T_c versus n for the Ethers are plotted on Figure 9 from which:

$$T_b/T_c \text{ at } n = 0 \quad = 2H + 0 = 0.5915 \qquad \text{Hence } \underline{0. = 0.0165}$$

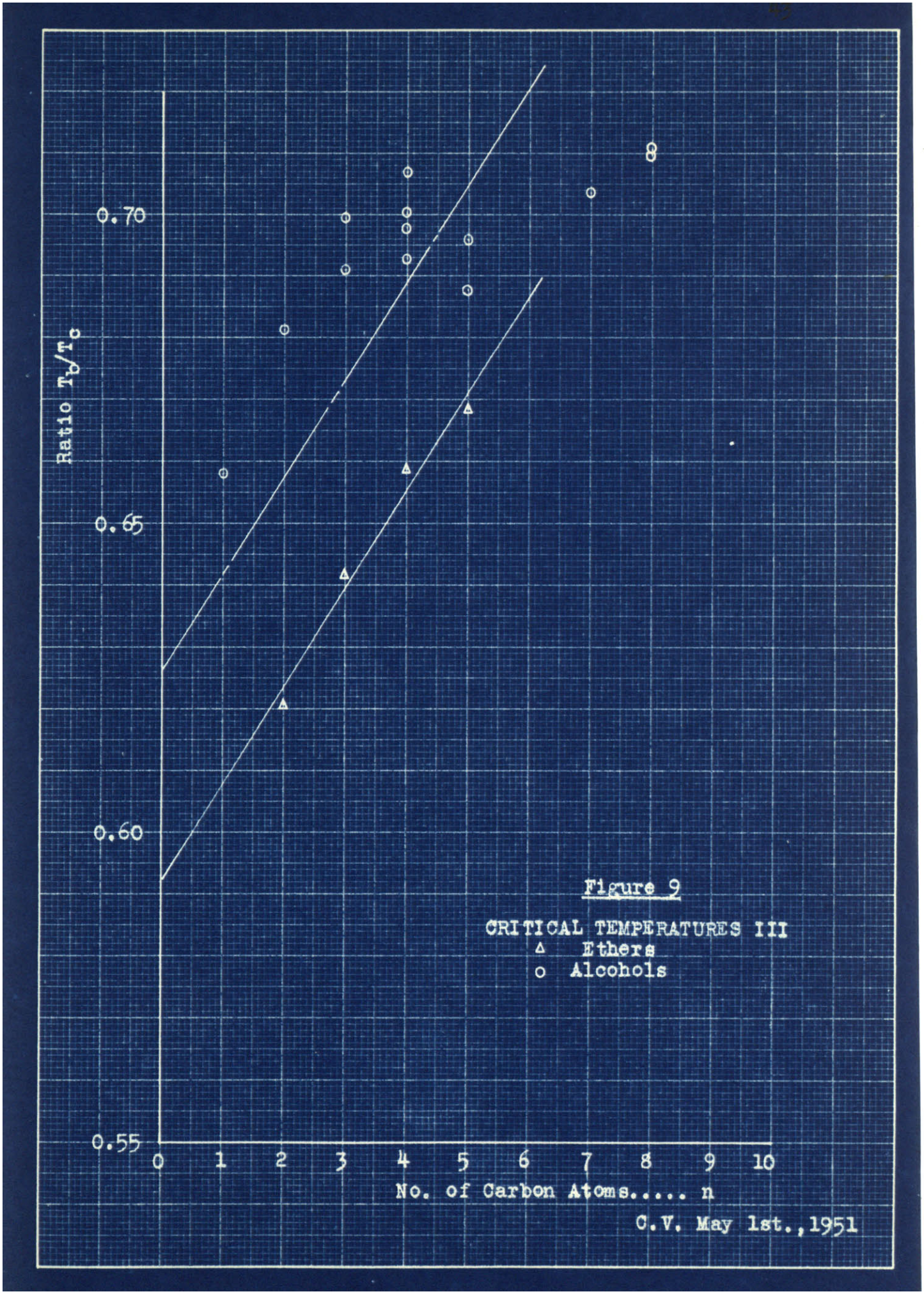

Figure 9

CRITICAL TEMPERATURES III

△ Ethers

○ Alcohols

TABLE XV

Critical Temperatures of the Esters

Compounds	Exp'l T_b	Exp'l T_c	Exp'l T_b/T_c	n	Calc'd T_b/T_c	Calc'd T_c	Dev'n	% Dev'n
Methyl Formate	305.0	487.2	0.6260	2	0.6286	486.0	- 1.2	- 0.2
Ethyl Formate	327.5	508.5	0.6441	3	0.6444	509.0	+ 0.5	+ 0.1
Propyl Formate	354.5	538.0	0.6589	4	0.6602	537.0	- 1.0	- 0.2
Isobutyl Formate	371.4	551.2	0.6738	5	0.6760	550.0	- 1.2	- 0.2
Isoamyl Formate	396.7	576.2	0.6885	6	0.6918	574.0	- 2.2	- 0.4
Methyl Acetate	330.3	506.9	0.6516	3	0.6444	513.0	+ 6.1	+ 1.2
Ethyl Acetate	350.3	523.2	0.6695	4	0.6602	531.0	+ 7.8	+ 1.5
Propyl Acetate	374.8	549.4	0.6822	5	0.6760	555.0	+ 5.6	+ 1.0
n-Butyl Acetate	399.7	579.2	0.6901	6	0.6918	578.0	- 1.2	- 0.2
Isoamyl Acetate	415.7	599.2	0.6938	7	0.7076	588.0	-11.2	- 1.9
Methyl Propionate	353.1	530.6	0.6655	4	0.6602	535.0	+ 4.4	+ 0.8
Ethyl Propionate	372.3	546.1	0.6817	5	0.6760	551.0	+ 4.9	+ 0.9
Propyl Propionate	396.6	578.2	0.6859	6	0.6918	573.0	- 5.2	- 0.9

TABLE XV (Cont)

Compound	Exp'l T_b	Exp'l T_c	Exp'l T_b/T_c	n	Calc'd T_b/T_c	Calc'd T_c	Dev'n	% Dev'n
Isobutyl Propionate	411.2	592.2	0.6944	7	0.7076	582.0	-10.2	- 1.7
Isoamyl Propionate	433.4	611.2	0.7091	8	0.7234	600.0	-11.2	- 1.8
Methyl Butyrate	375.5	554.5	0.6772	5	0.6760	556.0	+ 1.5	+ 0.3
Methyl Isobutyrate	365.8	540.7	0.6765	5	0.6760	541.0	+ 0.3	+ 0.1
Ethyl Butyrate	394.5	566.2	0.6968	6	0.6918	570.0	+ 3.8	+ 0.7
Ethyl Isobutyrate	384.9	553.2	0.6958	6	0.6918	556.0	+ 2.8	+ 0.5
Propyl Butyrate	416.2	600.2	0.6934	7	0.7076	588.0	-12.2	- 2.0
Propyl Isobutyrate	408.6	589.2	0.6935	7	0.7076	577.5	-11.7	- 2.0
Isobutyl Isobutyrate	421.9	602.2	0.7006	8	0.7234	584.0	-18.2	- 3.0
Isoamyl Isobutyrate	451.8	619.2	0.7279	9	0.7392	613.0	- 6.2	- 1.0
Methyl Valerate	400.5	567.2	0.7061	6	0.6918	579.0	+11.8	+ 2.1
Ethyl Valerate	418.7	570.2	0.7343	7	0.7076	592.0	+21.8	+ 3.8
Ethyl Isovalerate	408.2	588.2	0.6934	7	0.7076	578.0	-10.2	- 1.7
Propyl Isovalerate	429.1	609.2	0.7044	8	0.7234	594.0	-15.2	- 2.5
Isobutyl Isovalerate	441.7	621.2	0.7110	9	0.7392	600.0	-21.2	- 3.4

Experimental values of T_b/T_c versus n for the Esters are plotted on Figure 10 from which:

$$T_b/T_c \text{ at } n = 0 \quad = 2 \times 0 + D_{co} = 0.5970$$

Hence $\underline{D_{co} = 0.5640}$

This value for D_{co} is equal to that obtained for D_{cc}.

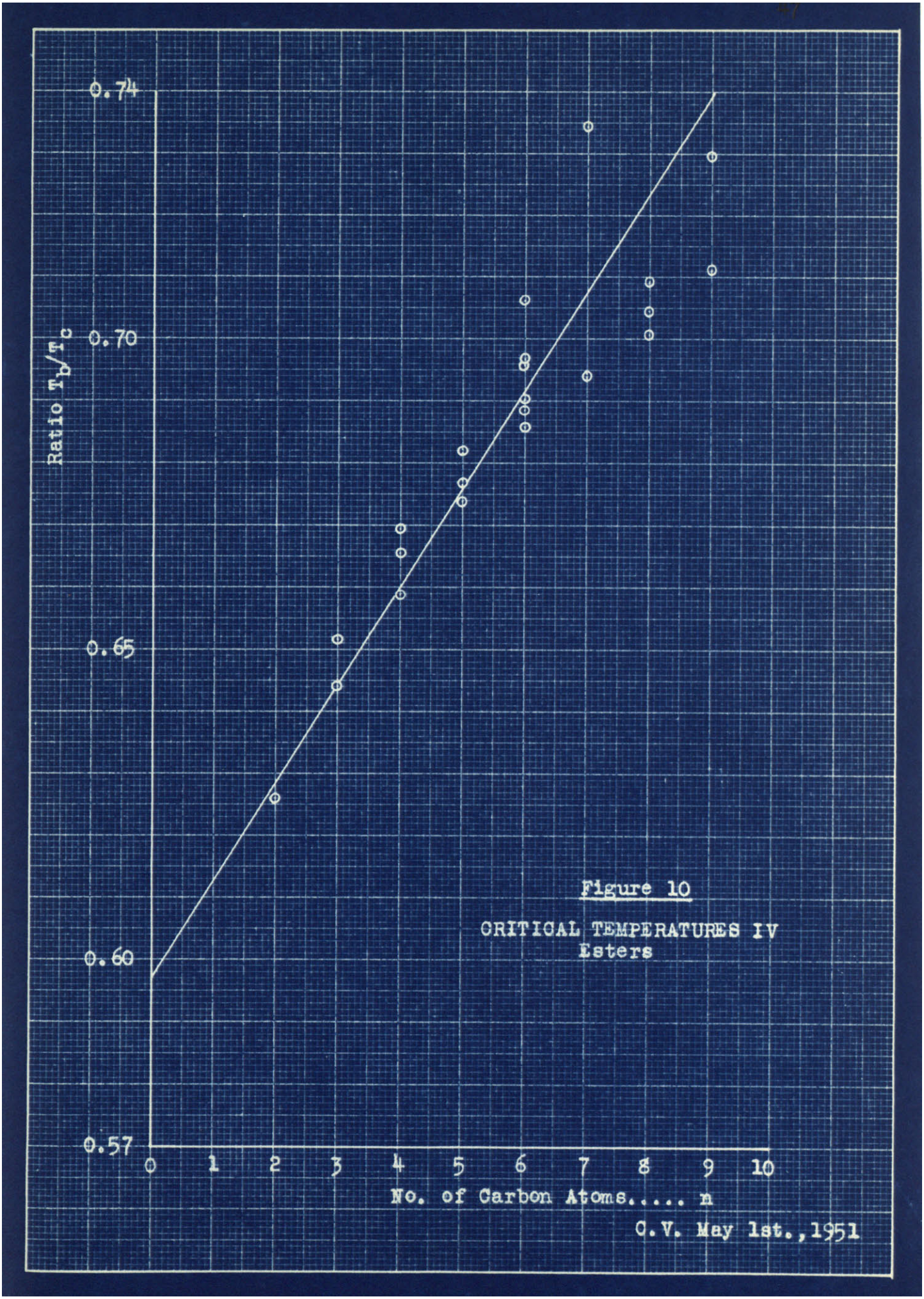

Figure 10

CRITICAL TEMPERATURES IV
Esters

TABLE XVI

Critical Temperatures of the Carboxylic Acids

Compound	Exp'l T_b	Exp'l T_c	Exp'l T_b/T_c	n	Calc'd T_b/T_c	Calc'd T_c	Dev'n	% Dev'n
Acetic Acid	391.3	594.8	0.6579	2	0.6628	590.0	- 4.8	- 0.8
Propionic Acid	414.3	611.7	0.6773	3	0.6786	611.0	- 0.7	- 0.1
n-Butyric Acid	436.7	628.2	0.6952	4	0.6944	631.0	+ 2.8	+ 0.4
i-Butyric Acid	427.6	609.2	0.7019	4	0.6944	616.0	+ 6.8	+ 1.1
n-Valeric Acid	460.2	652.2	0.7056	5	0.7102	648.0	- 4.2	- 0.6
i-Valeric Acid	449.9	634.2	0.7094	5	0.7102	633.0	- 1.2	- 0.2

Experimental values of T_b/T_c versus n for the Carboxylic Acids are plotted on Figure 11 from which:

$$T_b/T_c \text{ at } n = 0 \quad = D_{CO} + O + (OH) - H = 0.6312$$

Hence $\underline{(OH) = 0.3382}$

TABLE XVII

Critical Temperatures of the Alcohols

Compound	Exp'l T_b	Exp'l T_c	Exp'l T_b/T_c	n	Calc'd T_b/T_c	Calc'd T_c	Dev'n	% Dev'n
Methyl Alcohol	337.7	513.2	0.6580	1	0.6405	527.0	+13.8	+ 2.7
Ethyl Alcohol	351.7	516.3	0.6812	2	0.6563	535.0	+18.7	+ 3.6
n-Propyl Alcohol	371.0	536.9	0.6910	3	0.6721	552.0	+15.1	+ 2.8
i-Propyl Alcohol	355.5	508.2	0.6995	3	0.6721	529.0	+20.8	+ 4.1
n-Butyl Alcohol	390.9	560.2	0.6978	4	0.6879	569.0	+ 8.8	+ 1.6
i-Butyl Alcohol	380.5	538.2	0.7070	4	0.6879	554.0	+15.8	+ 2.9
sec-Butyl Alcohol	372.8	538.2	0.6927	4	0.6879	542.5	+ 4.3	+ 0.8
tert-Butyl Alcohol	356.0	508.2	0.7005	4	0.6879	518.0	+ 9.8	+ 1.9
i-Amyl Alcohol	403.7	580.2	0.6958	5	0.7037	574.0	- 6.2	- 1.1
tert-Amyl Alcohol	375.0	545.2	0.6878	5	0.7037	533.0	-12.2	- 2.2
n-Heptyl Alcohol	449.0	638.2	0.7035	7	0.7353	611.0	-27.2	- 4.3
n-Octyl Alcohol	467.2	658.2	0.7098	8	0.7511	622.0	-36.2	- 5.5
sec-Octyl Alcohol	452.7	637.2	0.7105	8	0.7511	603.0	-34.2	- 5.4

TABLE XVIII

Critical Temperatures of the Amines

Compound	Exp'l T_b	Exp'l T_c	Exp'l T_b/T_c	n	Calc'd T_b/T_c	Calc'd T_c	Dev'n	% Dev'n
Methylamine	266.7	430.1	0.6201	1	0.6158	433.0	+ 2.9	+ 0.7
Ethylamine	289.8	456.4	0.6350	2	0.6316	459.0	+ 2.6	+ 0.6
Propylamine	321.9	497.0	0.6477	3	0.6474	497.0	0.0	0.0
Dimethylamine	280.6	437.8	0.6409	2	0.6316	444.0	+ 6.2	+ 1.4
Diethylamine	329.2	496.7	0.6628	4	0.6632	496.5	- 0.2	0.0
Dipropylamine	383.9	550.2	0.6977	6	0.6948	552.0	+ 1.8	+ 0.3
Trimethylamine	276.7	434.2	0.6373	3	0.6474	427.0	- 7.2	- 1.7
Triethylamine	362.7	535.2	0.6777	6	0.6948	522.0	-13.2	- 2.5
Aniline	457.6	699.2	-	-	0.6534	700.0	+ 0.8	+ 0.1
Methyl Aniline	468.9	702.2	-	-	0.6692	702.0	- 0.2	0.0
Dimethyl Aniline	466.7	688.2	-	-	0.6850	682.0	- 6.2	- 0.9

Experimental values of T_b/T_c versus n for the Amines are plotted on Figure 11 from which:

T_b/T_c at $n = 0 \quad = 3H + N$ Hence $\underline{N = - 0.2625}$

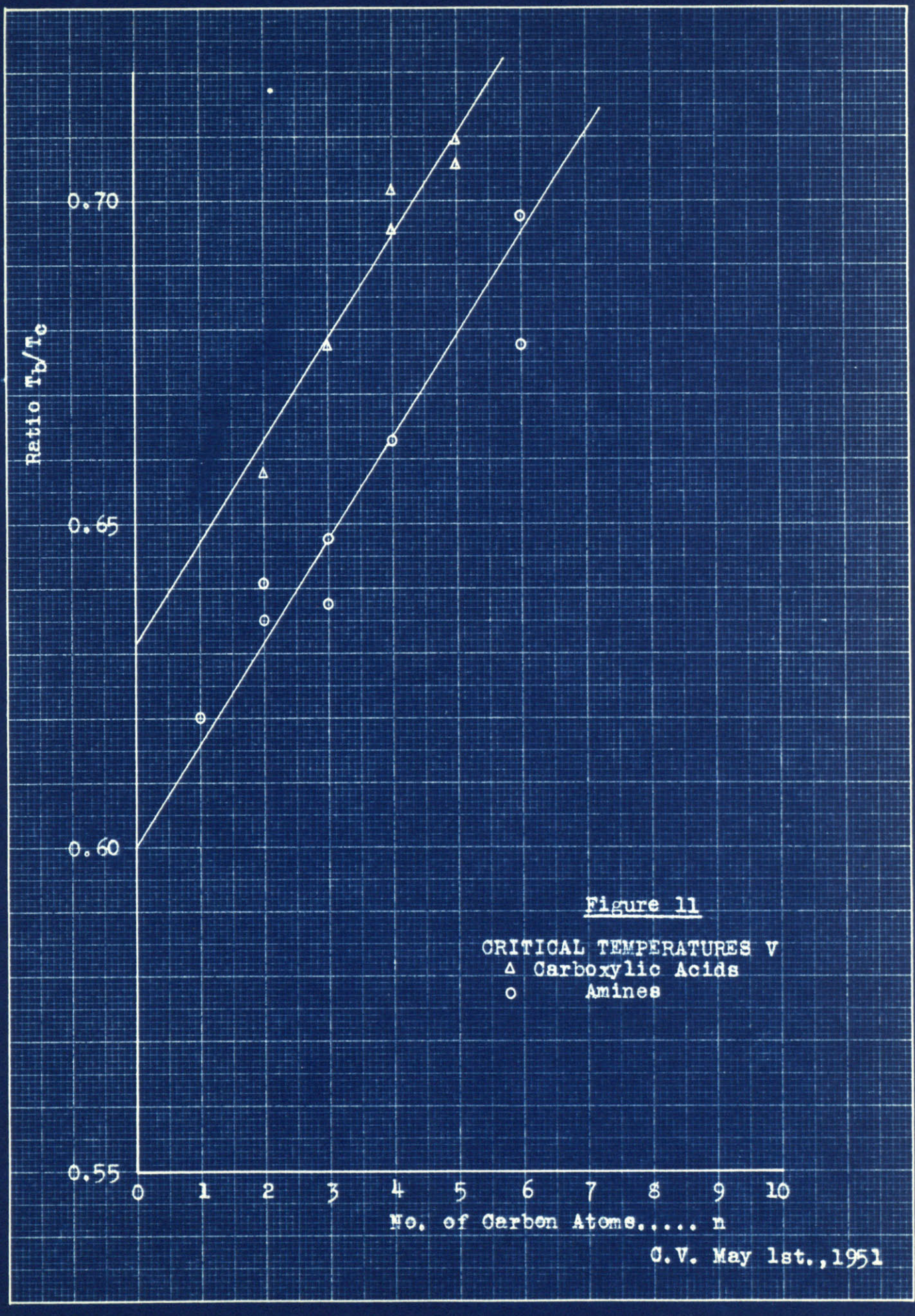

Figure 11

CRITICAL TEMPERATURES V
△ Carboxylic Acids
○ Amines

C.V. May 1st., 1951

TABLE XIX

Critical Temperatures of the Nitriles

Compound	Exp'l T_b	Exp'l T_c	Exp'l T_b/T_c	n	Calc'd T_b/T_c	Calc'd T_c	Dev'n	% Dev'n
Acetonitrile	355.2	547.9	0.6483	2	0.6406	555.0	+ 7.1	+ 1.3
Propionitrile	370.3	564.4	0.6561	3	0.6564	564.0	- 0.4	- 0.1
Butyronitrile	391.2	582.2	0.6719	4	0.6722	582.0	- 0.2	0.0
Capronitrile	436.2	622.2	0.7011	6	0.7038	620.0	- 2.2	- 0.4
Benzonitrile	463.9	699.2	0.6635	-	0.6782	685.0	-14.2	- 2.0

Experimental values of T_b/T_c versus n for the Nitriles are plotted on Figure 12 from which:

$$T_b/T_c \text{ at } n = 0 \quad = N + T_{cn} - H = 0.6090$$

Hence $\underline{T_{cn} = 1.1590}$

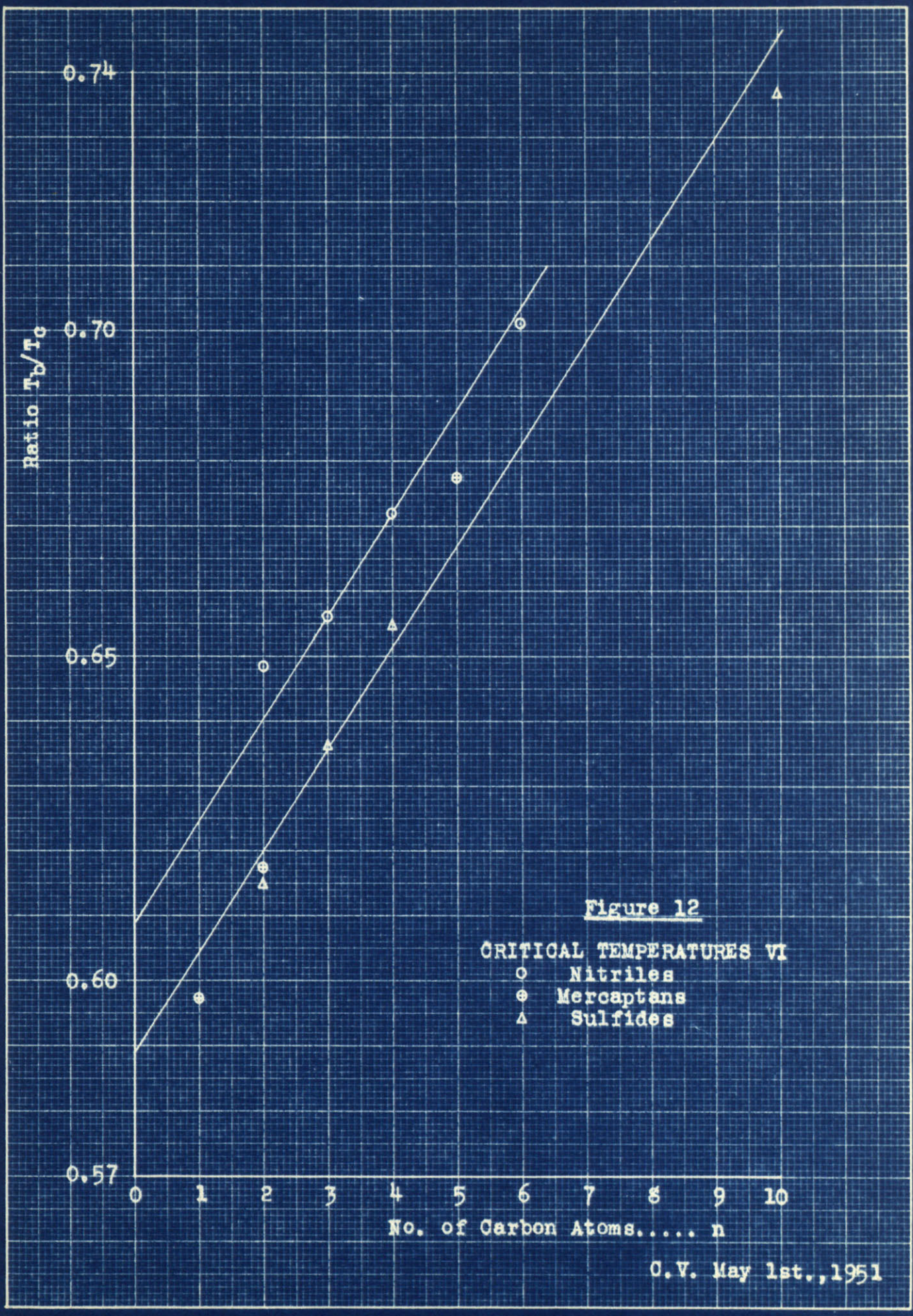
0.74
0.70
0.65
0.60
0.57
Ratio T_b/T_c
0 1 2 3 4 5 6 7 8 9 10
No. of Carbon Atoms..... n
Figure 12
CRITICAL TEMPERATURES VI
Nitriles
Mercaptans
Sulfides
C.V. May 1st., 1951

TABLE XX

Critical Temperatures of the Mercaptans and Sulfides

Compound	Exp'l T_b	Exp'l T_c	Exp'l T_b/T_c	n	Calc'd T_b/T_c	Calc'd T_c	Dev'n	% Dev'n
Methyl Mercaptan	280.8	470.0	0.5974	1	0.6048	465.0	- 5.0	- 1.1
Ethyl Mercaptan	307.9	498.7	0.6174	2	0.6206	496.0	- 2.7	- 0.5
Isoamyl Mercaptan	402.7	594.2	0.6777	5	0.6680	604.0	+ 9.8	+ 1.7
Methyl Sulfide	309.4	503.1	0.6150	2	0.6206	498.5	- 4.6	- 0.9
Methyl Ethyl Sulfide	339.2	533.2	0.6362	3	0.6364	532.0	- 1.2	- 0.2
Ethyl Sulfide	364.8	557.0	0.6549	4	0.6522	560.0	+ 3.0	+ 0.5
Isoamyl Sulfide	489.2	664.2	0.7365	10	0.7470	655.0	- 9.2	- 1.4
Ethyl Disulfide	426.7	642.2	-	-	0.6662	641.0	- 1.2	- 0.2

Experimental values of T_b/T_c versus n for the Mercaptans and Sulfides are plotted on Figure 12 from which:

T_b/T_c at n = 0 = 2H + S = 0.5890 Hence S = 0.0140

TABLE XXI

Critical Temperatures of the Acetylenes

Compound	Exp'l T_b	Exp'l T_c	Exp'l T_b/T_c	n	Calc'd T_b/T_c	Calc'd T_c	Dev'n	% Dev'n
Acetylene	189.6	312.9	0.6059	2	0.5981	317.0	+ 4.1	+ 1.3
Methyl Acetylene	245.7	394.8	0.6223	3	0.6139	400.0	+ 5.2	+ 1.3
Dimethyl Acetylene	302.1	488.7	0.6182	4	0.6297	480.0	- 8.7	- 1.8
Ethyl Acetylene	291.7	463.7	0.6291	4	0.6297	463.0	- 0.7	- 0.2
Propyl Acetylene	313.2	493.5	0.6347	5	0.6455	486.0	- 7.5	- 1.5

Experimental values of T_b/T_c versus n for the Acetylenes are plotted on Figure 13 from which:

$$T_b/T_c \text{ at } n = 0 \quad = T_{cc} - 2H = 0.5665 \qquad \text{Hence } \underline{T_{cc} = 1.1415}$$

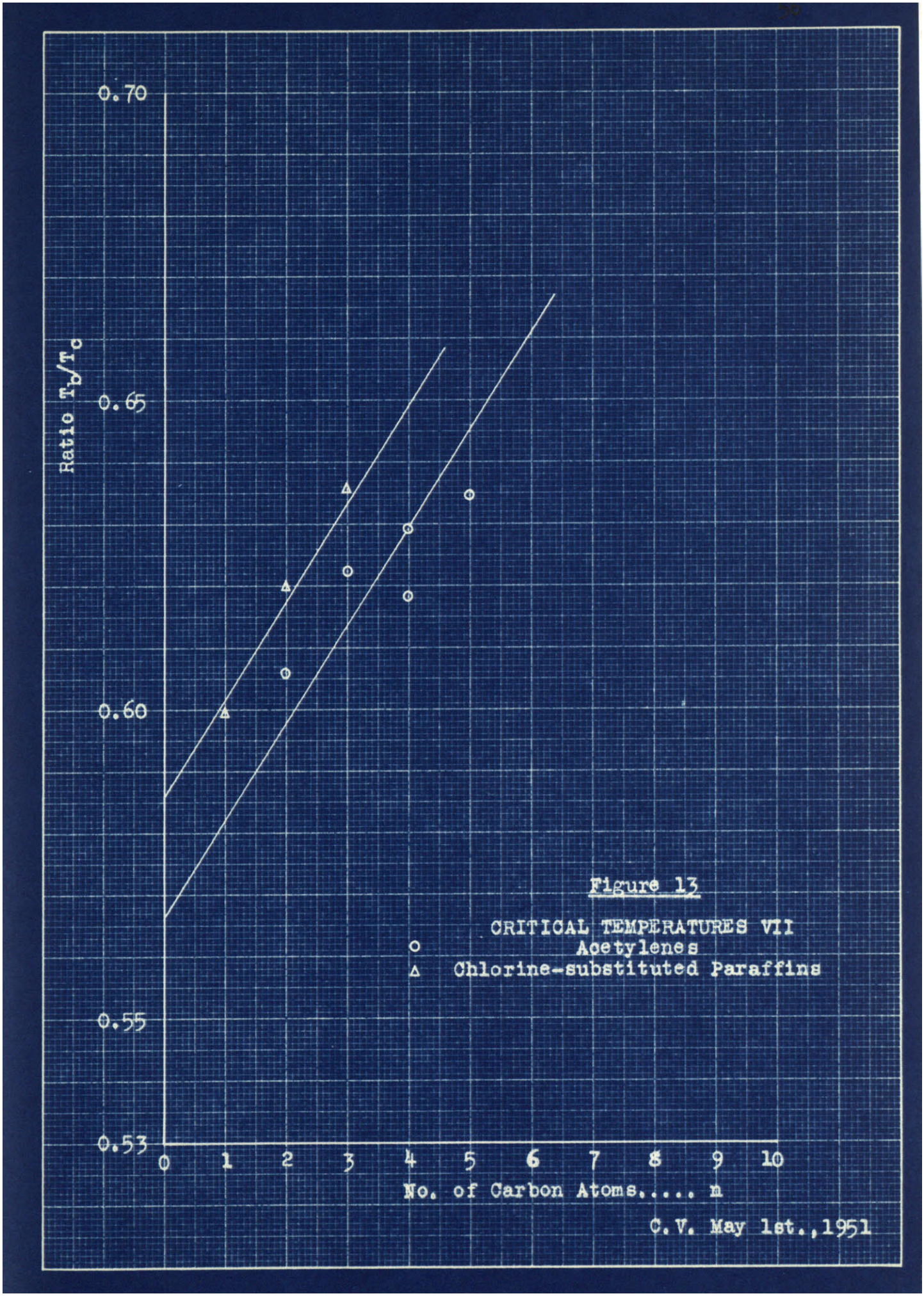

Figure 13

CRITICAL TEMPERATURES VII

○ Acetylenes

△ Chlorine-substituted Paraffins

For the remaining cases, there were not sufficient data to obtain elemental values of T_b/T_c by the graphical technique and it was necessary to revert to the method of calculating individual values for an element from each compound containing it for which experimental data were available. As in the case of Critical Volumes, an average of these calculated values was assumed for the element in question. The calculated values and the averages taken are presented in tabular form below.

Chloride-substituted Hydrocarbons

Compound	Exp'l T_b	Exp'l T_c	Exp'l T_b/T_c	Calc'd Cl
Carbon Tetrachloride	350.0	556.3	0.6292	0.2971
Chloroform	334.4	536.2	0.6236	0.2984
Methyl Chloride	249.5	416.3	0.5993	0.2960
Ethyl Chloride	285.4	460.4	0.6199	0.3008
n-Propyl Chloride	319.8	503.2	0.6355	0.3002
Chlorobenzene	405.3	632.2	0.6411	0.3006

From these results, the average value of 0.2983 has been assigned to chlorine. Hence Cl = 0.2983

Bromine-substituted Hydrocarbons

Compound	Exp'l T_b	Exp'l T_c	Exp'l T_b/T_c	Calc'd Br
Ethyl Bromide	311.2	504.2	0.6172	0.2981
Bromobenzene	429.4	670.2	0.6407	0.2998

From these results, the average value of 0.2990 has been assigned to bromine. Hence Br = 0.2990

Fluorine-substituted Hydrocarbons

Compound	Exp'l T_b	Exp'l T_c	Exp'l T_b/T_c	Calc'd F
Methyl Fluoride	195.2	318.1	0.6136	0.3103
Dichlorodifluoromethane	244.0	384.0	0.6343	0.3050
Fluorobenzene	359.2	559.2	0.6423	0.3014

From these results, the average value of 0.3042 has been assigned to fluorine. Hence F = 0.3042

Iodine-substituted Hydrocarbons

The experimental value of the Critical Temperature for only one of these compounds, that of Iodobenzene, is reported, but such excellent agreement was found for the other halogen-substituted hydrocarbons that a value for iodine has been calculated from this single result.

Iodobenzene: Normal Boiling Temperature = 461.8°K

Critical Temperature = 721.2°K

Hence T_b/T_c = 0.6403 and thus

I = 0.2994

TABLE XXII

Critical Temperatures of the Halogen-substituted Hydrocarbons

Compound	Exp'l T_b	Exp'l T_c	Calc'd T_b/T_c	Calc'd T_c	Dev'n	% Dev'n
Carbon Tetra-Chloride	350.0	556.3	0.6340	552.0	- 4.3	- 0.8
Chloroform	334.4	536.2	0.6232	537.0	+ 0.8	+ 0.2
Methyl Chloride	249.5	416.3	0.6016	415.0	- 1.3	- 0.3
Ethyl Chloride	285.4	460.4	0.6174	462.0	+ 1.6	+ 0.3
n-Propyl Chloride	319.8	503.2	0.6332	505.0	+ 1.8	+ 0.4
Chlorobenzene	405.3	632.2	0.6392	635.0	+ 2.8	+ 0.4
Ethyl Bromide	311.2	504.2	0.6181	504.0	- 0.2	0.0
Bromobenzene	429.4	670.2	0.6399	671.0	+ 0.8	+ 0.1
Methyl Fluoride	195.2	318.1	0.6075	321.0	+ 2.9	+ 0.9
Dichlorodi-fluoromethane	244.0	384.7	0.6458	378.0	- 6.7	- 1.7
Fluorobenzene	359.2	559.2	0.6451	557.0	- 2.2	- 0.4
Iodobenzene	461.8	721.2	0.6403	721.2	0.0	0.0

TABLE XXIII

Critical Temperatures of the Elements and Inorganic Compounds

Compounds	Exp'l T_b	Exp'l T_c	Calc'd T_b/T_c	Calc'd T_c	Dev'n	% Dev'n
Ammonia	239.8	405.6	0.6000	400.0	- 5.6	- 1.4
Carbon Monoxide	81.2	134.2	0.5988	136.0	+ 1.8	+ 1.3
Carbon Dioxide	194.7*	304.3	0.6018	323.0	+18.7	+ 6.2
Carbon Disulfide	319.5	546.2	0.5968	535.0	-11.2	- 2.1
Cyanogen	252.7	401.2	0.6746	375.0	-26.2	- 6.5
Fluorine	86.2	118.2	0.6094	141.8	+23.6	+20.0
Chlorine	238.6	417.2	0.5966	400.0	-17.2	- 4.1
Bromine	332.0	575.2	0.5980	555.0	-20.2	- 3.5
Iodine	457.6	826.2	0.5988	765.0	-61.2	- 7.4
Hydrogen	20.5	33.1	0.5750	35.7	+ 2.6	+ 7.8
Hydrogen Fluoride	292.6	503.4	0.5917	494.0	- 9.4	- 1.9
Hydrogen Chloride	188.2	324.6	0.5858	321.0	- 3.6	- 1.1
Hydrogen Bromide	206.2	363.2	0.5865	351.0	-12.2	- 3.4
Hydrogen Iodide	237.7	424.2	0.5869	404.0	-20.2	- 4.8
Hydrogen Sulfide	213.6	373.6	0.5890	363.0	-10.6	- 2.8
Hydrogen Cyanide	299.2	456.7	0.6348	479.0	+22.3	+ 4.9
Nitrogen	77.4	126.1	0.6340	122.2	- 3.9	- 3.1
Oxygen	90.2	154.4	0.5970	151.2	- 3.2	- 2.1
Water Vapor	373.2	647.2	0.5915	632.0	-15.2	- 2.4
Sulfur Dioxide	263.2	430.4	0.6110	431.0	+ 0.6	+ 0.1
Sulfur Trioxide	317.8	491.5	0.6275	507.0	+15.5	+ 3.2

* Carbon Dioxide sublimes at this temperature under atmospheric pressure.

TABLE XXIV

List of Atomic and Structural Values

--- Critical Temperatures

Atomic or Structural Element	Symbol	Value
Carbon	C	- 0.5592
Hydrogen	H	0.2875
Oxygen	O	0.0165
(OH) Group	(OH)	0.3382
Nitrogen	N	- 0.2625
Sulfur	S	0.0140
Fluorine	F	.0.3042
Chlorine	Cl	0.2983
Bromine	Br	0.2990
Iodine	I	.0.2994
Double Bond (C=C)	D_{cc}	0.5640
Double Bond (C=O)	D_{co}	0.5640
Double Bond (C=S)	D_{cs}	0.5640
Double Bond (S=O)	D_{so}	0.5640
Triple Bond (C≡C)	T_{cc}	1.1415
Triple Bond (C≡N)	T_{cn}	1.1590
Triple Bond (N≡N)	T_{nn}	1.1590
Six-Membered Ring (Aromatic and Naphthenic	R_6	0.5666

(3) CRITICAL PRESSURES

Experimental and calculated data are again presented in both tabular and graphical form as in the previous cases.

The first two columns of the tables contain the experimentally determined critical temperatures and pressures in degrees Kelvin and atmospheres respectively. Following these are the ratios T_c/P_c^a and n, the number of carbon atoms in the molecule. From these two columns the graphs of T_c/P_c^a versus n have been plotted from which, in turn, the various elemental values were obtained. The remaining columns contain the calculated value of T_c/P_c^a, the calculated critical pressure, the deviation of the calculated from the experimental value and this deviation expressed as a percentage of the experimental value.

In each case the value of the exponent "a" is presented at the foot of the tables.

TABLE XXV

Critical Pressures of the Paraffin Hydrocarbons

Compound	Exp'l T_c	Exp'l P_c	Exp'l T_c/P_c^a	n	Calc'd T_c/P_c^a	Calc'd P_c	Dev'n	% Dev'n
Methane	190.7	45.8	8.95	1	8.82	46.6	+ 0.8	+ 1.8
Ethane	305.3	48.8	13.61	2	13.74	48.2	- 0.6	- 1.2
Propane	370.2	42.0	18.61	3	18.66	41.9	- 0.1	- 0.3
Butane	425.2	37.47	23.42	4	23.58	37.2	- 0.3	- 0.8
Pentane	470.4	33.0	28.69	5	28.50	33.3	+ 0.3	+ 0.9
Hexane	507.1	30.0	33.37	6	33.42	30.0	0.0	0.0
Heptane	542.7	27.6	38.19	7	38.34	27.5	- 0.1	- 0.4
Octane	573.1	25.2	43.37	8	43.26	25.3	+ 0.1	+ 0.4

The value for the exponent "a" for this series is 0.80

Experimental values of T_c/P_c^a versus n for the Paraffin Hydrocarbons are plotted on Figure 14 from which:

Slope of Curve = C + 2H = 4.92) Hence C = 1.02

T_c/P_c^a at n = 0 2H = 3.90) H = 1.95

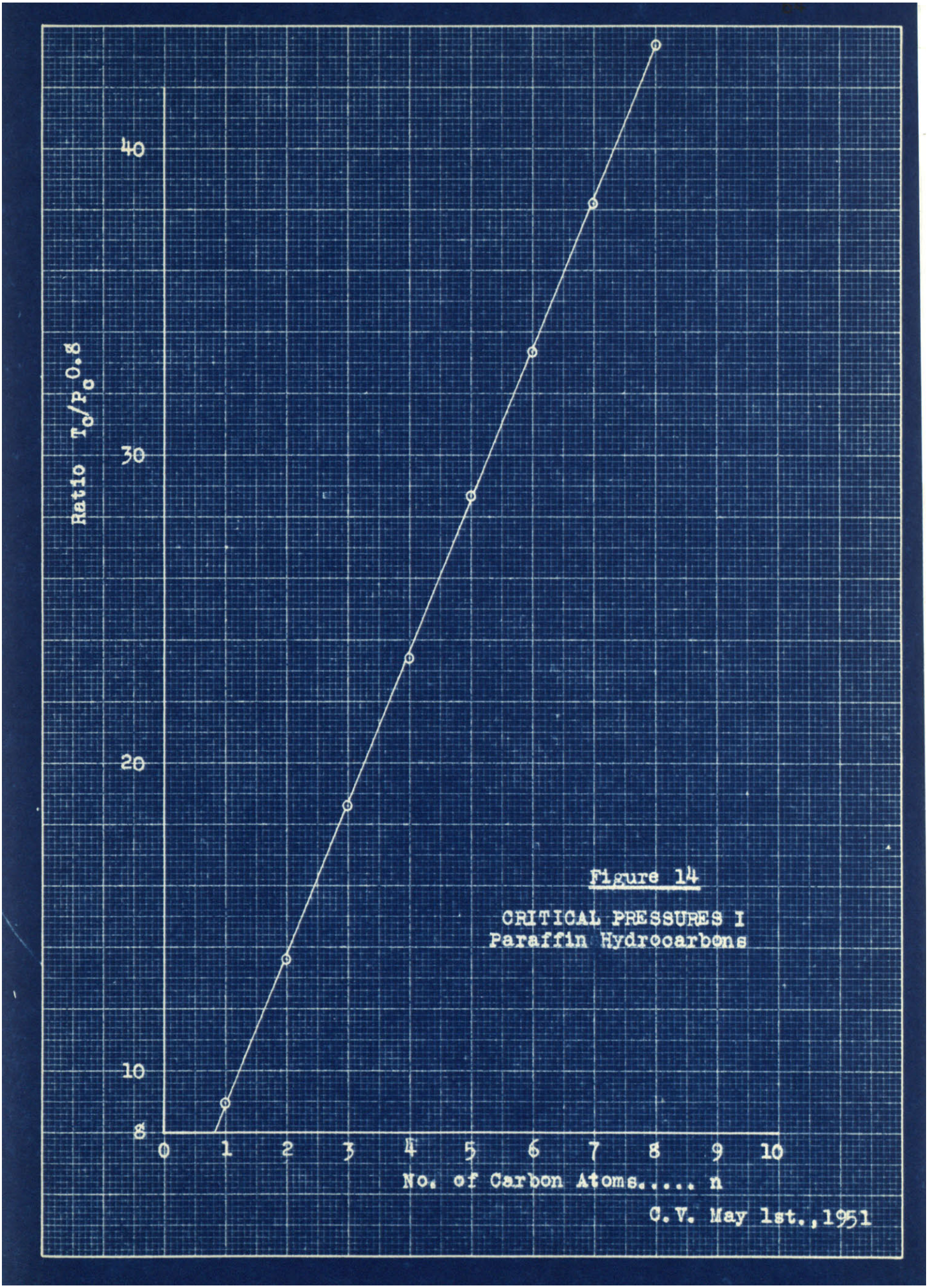

Figure 14

CRITICAL PRESSURES I
Paraffin Hydrocarbons

TABLE XXVI

Critical Pressures of the Olefins and Diolefins

Compound	Exp'l T_c	Exp'l P_c	Exp'l T_c/P_c^a	n	Calc'd T_c/P_c^a	Calc'd P_c	Dev'n	% Dev'n
Ethylene	283.1	50.9	12.21	2	12.34	51.16	+ 0.26	+ 0.5
Propylene	365.3	45.0	17.38	3	17.26	45.50	+ 0.40	+ 0.9
Pentene-1	474.4	40.4	24.61	5	27.10	35.81	- 4.49	-11.4
3-Methylbutene-1	464.8	33.9	27.73	5	27.10	34.89	+ 0.99	+ 2.9
Butadiene-1,3	425.2	42.7	-	-	20.78	43.40	+ 0.70	+ 1.6

The value of the exponent "a" for this series is 0.80

Experimental values of T_c/P_c^a versus n for the Olefins are plotted on Figure 15 from which:

$$T_c/P_c^a \text{ at } n = 0 \quad = \quad \underline{D_{cc} = 2.5}$$

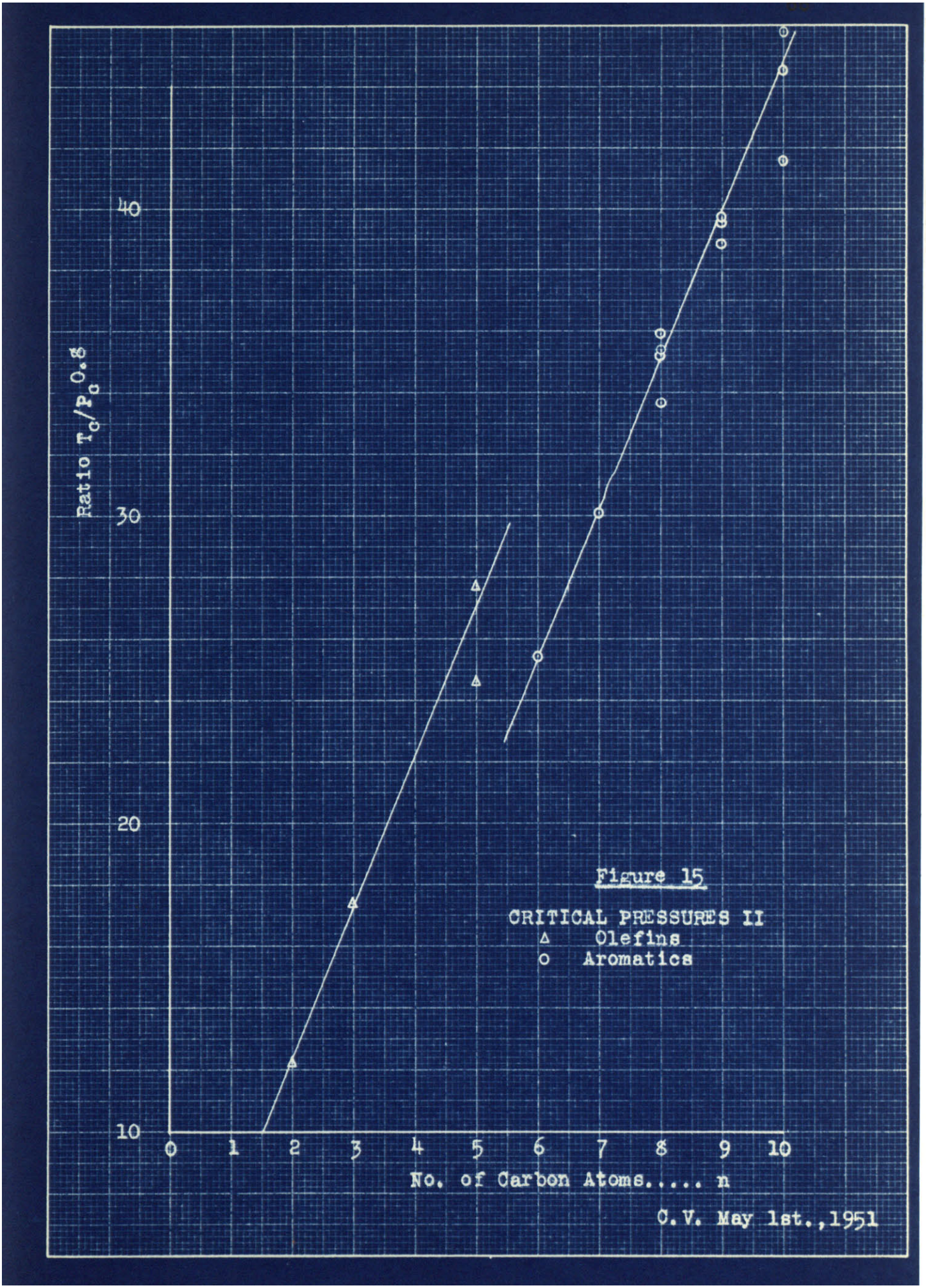

Figure 15

CRITICAL PRESSURES II
△ Olefins
○ Aromatics

TABLE XXVII

Critical Pressures of the Aromatics

Compound	Exp'l T_c	Exp'l P_c	Exp'l T_c/P_c^a	n	Calc'd T_c/P_c^a	Calc'd P_c	Dev'n	% Dev'n
Benzene	561.7	47.9	25.43	6	25.18	48.5	+ 0.6	+ 1.2
Toluene	593.8	41.6	30.09	7	30.10	41.6	0.0	0.0
o-Xylene	631.5	36.9	35.22	8	35.02	37.1	+ 0.2	+ 0.5
m-Xylene	618.8	35.8	35.36	8	35.02	36.2	+ 0.4	+ 1.0
p-Xylene	617.6	35.0	35.92	8	35.02	36.1	+ 1.1	+ 3.1
Ethyl Benzene	619.2	38.1	33.66	8	35.02	36.3	- 1.8	- 4.7
1,2,4-Trimethyl Benzene	654.4	33.2	39.72	9	39.94	33.0	- 0.2	- 0.6
1,3,5-Trimethyl Benzene	640.2	33.2	38.86	9	39.94	32.1	- 1.1	- 3.3
Propyl Benzene	638.8	32.3	39.62	9	39.94	32.0	- 0.3	- 0.9
Isopropyl Benzene	635.9	32.2	39.55	9	39.94	31.8	- 0.4	- 1.2
1-Methyl-2-isopropyl Benzene	651.8	28.6	44.57	10	44.86	28.4	- 0.2	- 0.7
1-Methyl-4-isopropyl Benzene	651.8	28.6	44.57	10	44.86	28.4	- 0.2	- 0.7
1,2,4,5-Tetramethyl Benzene	675.7	28.6	46.20	10	44.86	29.7	+ 1.1	+ 3.8
Isobutyl Benzene	650.2	31.1	41.58	10	44.86	28.3	- 2.8	- 9.0

The value of the exponent "a" for this series is 0.80.

Experimental values of T_c/P_c^a versus n for the Aromatics are plotted on Figure 15, from which:

T_c/P_c^a at n = 0 $= 3D_{cc} + R_6 - 6H = -4.34$ Hence $\underline{R_6 = -0.14}$

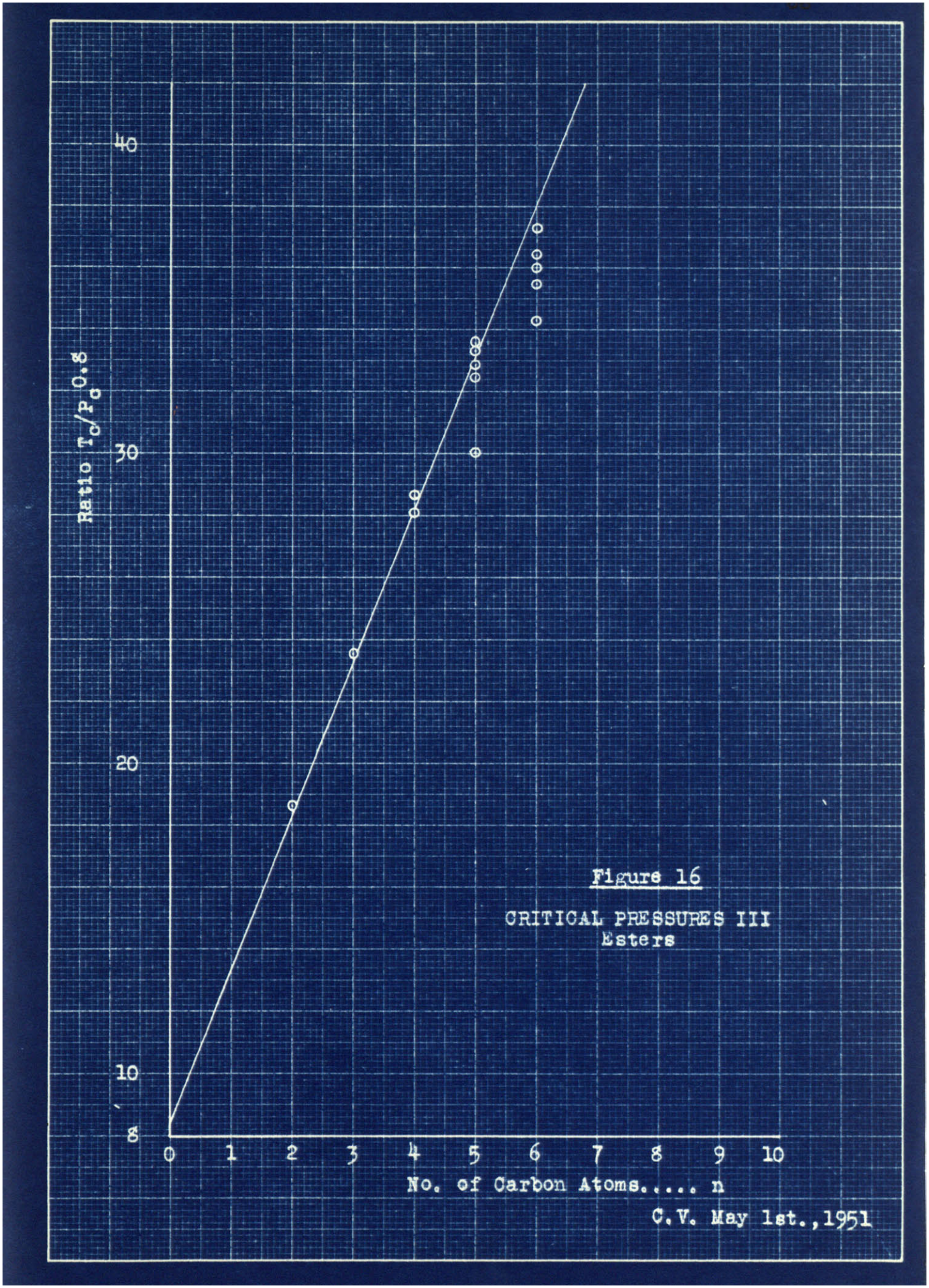

Figure 16

CRITICAL PRESSURES III
Esters

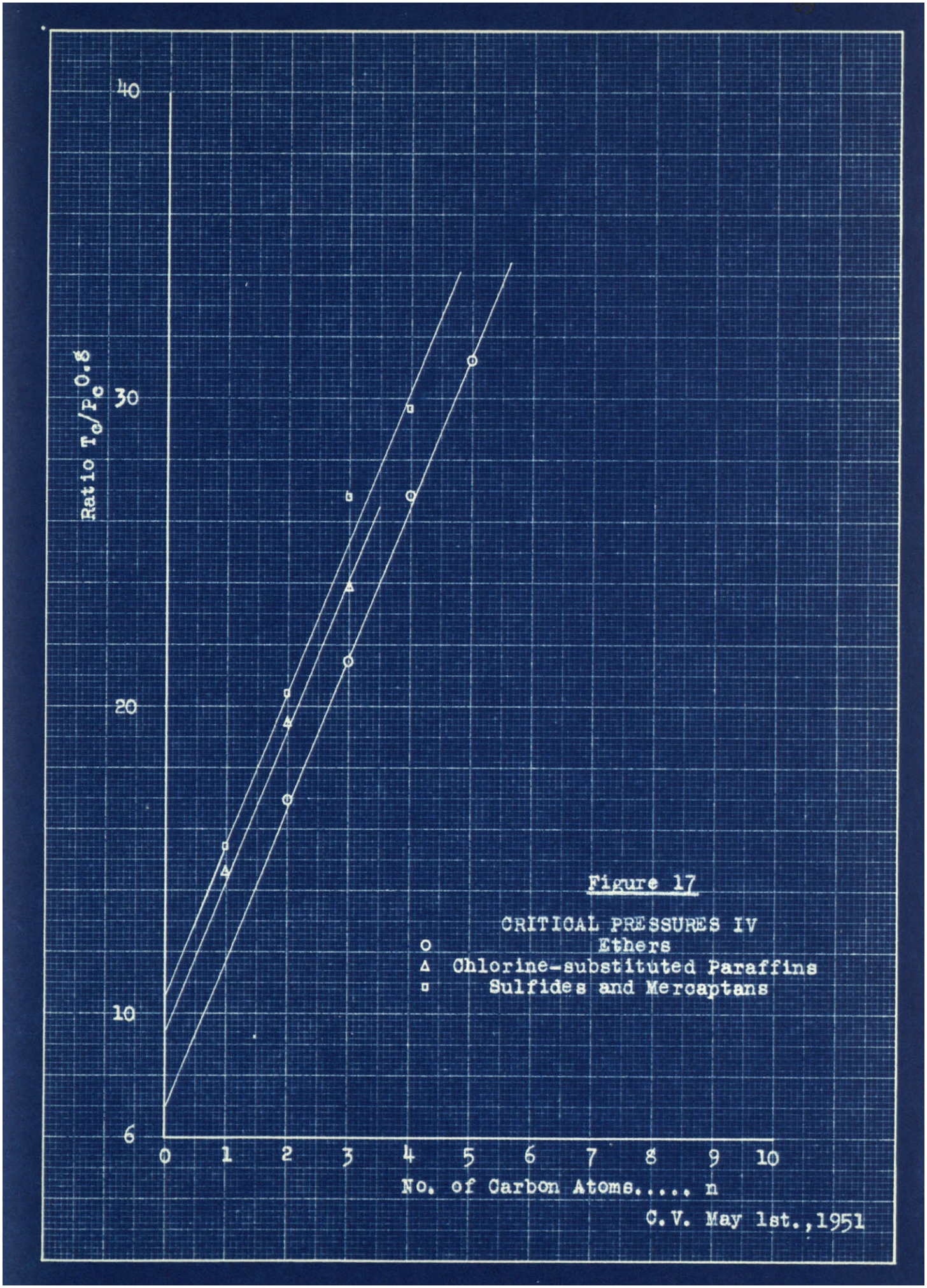

Figure 17

CRITICAL PRESSURES IV

○ Ethers

△ Chlorine-substituted Paraffins

▫ Sulfides and Mercaptans

TABLE XXVIII

Critical Pressures of the Ethers

Compound	Exp'l T_c	Exp'l P_c	Exp'l T_c/P_c^a	n	Calc'd T_c/P_c^a	Calc'd P_c	Dev'n	% Dev'n
Methyl Ether	400.1	52.0	16.96	2	16.74	52.8	+ 0.8	+ 1.5
Methyl Ethyl Ether	437.9	43.4	21.45	3	21.66	42.9	- 0.5	- 1.1
Ethyl Ether	467.0	35.5	26.86	4	26.58	36.0	+ 0.5	+ 1.4
Ethyl Propyl Ether	500.6	32.1	31.21	5	31.50	31.7	- 0.4	- 1.2

The value of the exponent for this series is 0.80.

The experimental values of T_c/P_c^a versus n for the Ethers are plotted on Figure 17, from which:

T_c/P_c^a at n = 0 = 2H + 0 = 6.9 Hence $\underline{0 = 3.0}$

TABLE XXIX

Critical Pressures of the Esters

Compound	Exp'l T_c	Exp'l P_c	Exp'l T_c/P_c^a	n	Calc'd T_c/P_c^a	Calc'd P_c	Dev'n	% Dev'n
Methyl Formate	487.2	59.1	18.64	2	18.34	60.3	+ 0.4	+ 0.7
Ethyl Formate	508.5	46.6	23.53	3	23.26	47.3	+ 0.7	+ 1.5
Propyl Formate	538.0	40.1	28.07	4	28.18	39.9	- 0.2	- 0.5
Isobutyl Formate	551.2	38.0	30.03	5	33.10	33.7	- 4.3	-11.0
Isoamyl Formate	576.2	34.0	34.31	6	38.02	29.9	- 4.1	-12.0
Methyl Acetate	506.9	46.3	23.58	3	23.26	47.1	+ 0.8	+ 1.7
Ethyl Acetate	523.2	37.8	28.63	4	28.18	38.5	+ 0.7	+ 1.9
Propyl Acetate	549.4	32.9	33.58	5	33.10	33.5	+ 0.6	+ 1.8
Isobutyl Acetate	561.2	31.0	35.98	6	38.02	28.9	- 2.1	- 6.8
Methyl Propionate	530.6	39.3	28.14	4	28.18	39.2	- 0.1	- 0.3
Ethyl Propionate	546.1	33.0	33.31	5	33.10	33.3	+ 0.3	+ 0.9
Methyl Butyrate	554.5	34.2	32.86	5	33.10	33.9	- 0.3	- 0.9
Ethyl Butyrate	566.2	30.0	37.27	6	38.02	29.3	- 0.7	- 2.3
Methyl Isobutyrate	540.7	33.7	32.43	5	33.10	32.9	- 0.8	- 2.4
Ethyl Isobutyrate	553.2	30.0	36.41	6	38.02	28.4	- 1.6	- 5.3
Methyl Valerate	567.2	32.0	35.46	6	38.02	29.3	- 2.7	- 8.4

The value of the exponent "a" for this series is 0.80

Experimental values of T_c/P_c^a versus n for the Esters are plotted on Figure 16, from which:

T_c/P_c^a at n = 0 $= D_{co} + 2x0 = 8.5$ Hence $\underline{D_{co} = 2.5}$

TABLE XXX

Critical Pressures of the Amines

Compound	Exp'l T_c	Exp'l P_c	Exp'l T_c/P_c^a	n	Calc'd T_c/P_c^a	Calc'd P_c	Dev'n	% Dev'n
Methylamine	430.1	73.6	13.80	1	13.22	77.7	+ 4.1	+ 5.5
Ethylamine	456.4	55.5	18.37	2	18.14	56.4	+ 0.9	+ 1.6
Propylamine	497.0	46.3	23.12	3	23.06	46.4	+ 0.1	+ 0.2
Dimethylamine	437.8	51.7	18.64	2	18.14	53.5	+ 1.8	+ 3.5
Diethylamine	496.7	36.2	28.13	4	27.98	36.4	+ 0.2	+ 0.6
Dipropylamine	550.2	31.0	35.28	6	37.82	28.4	- 2.6	- 8.4
Trimethylamine	434.2	41.0	22.26	3	23.06	39.2	- 1.8	- 4.4
Triethylamine	535.2	30.0	35.23	6	37.82	27.5	- 2.5	- 8.3

The value of the exponent "a" for this series is 0.80

Experimental values of T_c/P_c^a versus n for the Amines are plotted on Figure 18 from which:

T_c/P_c^a at n = 0 = 3H + N = 8.3 Hence N = 2.45

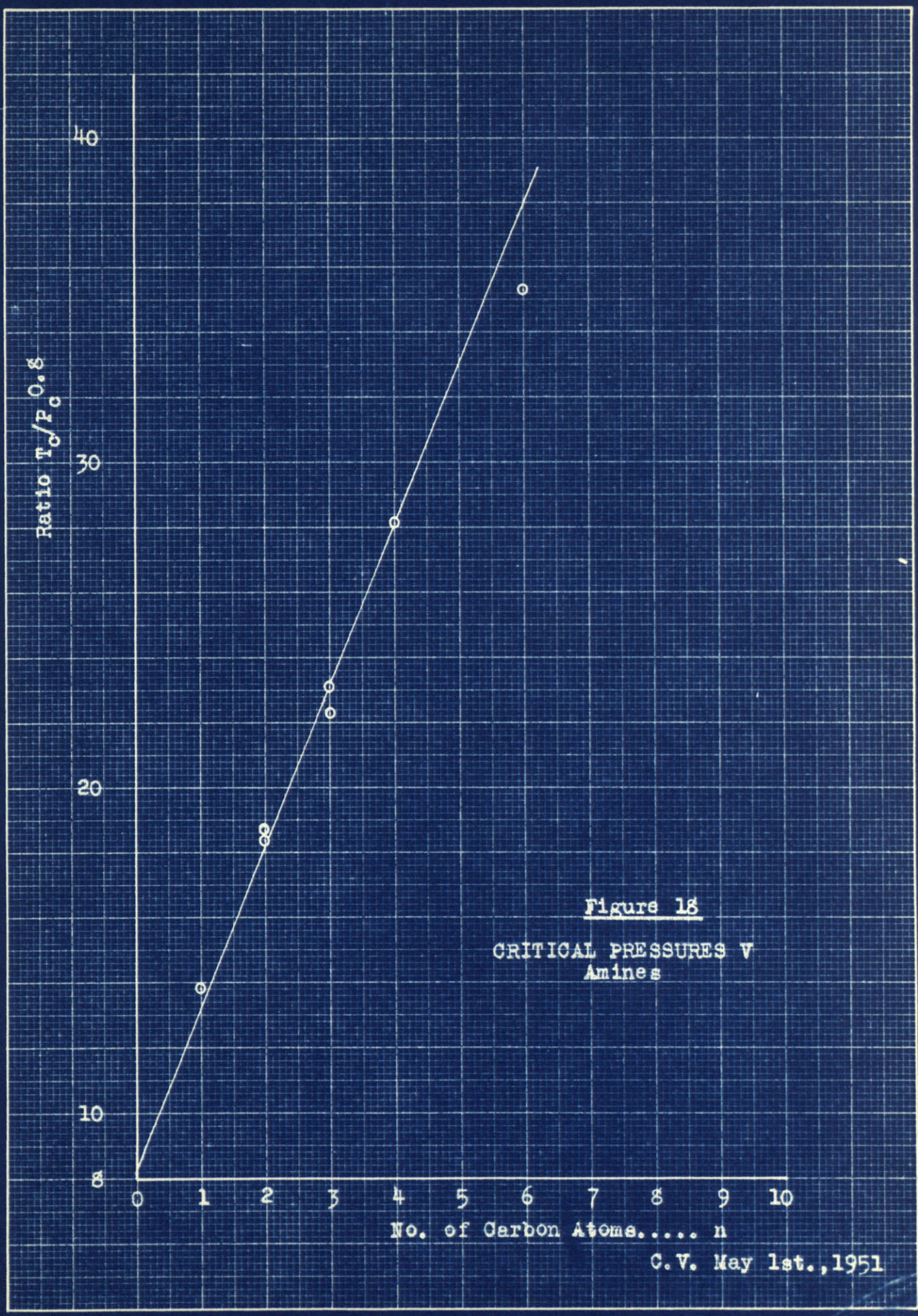

Figure 18

CRITICAL PRESSURES V
Amines

C.V. May 1st., 1951

TABLE XXXI

Critical Pressures of Sulfides and Mercaptans

Compound	Exp'l T_c	Exp'l P_c	Exp'l T_c/P_c^a	n	Calc'd T_c/P_c^a	Calc'd P_c	Dev'n	% Dev'n
Methyl Mercaptan	470.0	71.4	15.45	1	15.52	71.0	- 0.4	- 0.6
Ethyl Mercaptan	498.7	54.2	20.45	2	20.44	54.2	0.0	0.0
Methyl Sulfide	503.1	54.6	20.50	2	20.44	54.8	+ 0.2	+ 0.4
Methyl Ethyl Sulfide	533.2	42.0	26.81	3	25.36	44.9	+ 2.9	+ 6.9
Ethyl Sulfide	557.0	39.1	29.66	4	30.28	38.1	- 1.0	- 2.6

The value of the exponent "a" for this series is 0.80

Experimental values of T_c/P_c^a versus n for the Sulfides and Mercaptans are plotted on Figure 17, from which:

T_c/P_c^a at n = 0 = 2H + S = 10.6 Hence S = 6.7

TABLE XXXII

Critical Pressures of the Chlorine-substituted Paraffins

Compound	Exp'l T_c	Exp'l P_c	Exp'l T_c/P_c^a	n	Calc'd T_c/P_c^a	Calc'd P_c	Dev'n	% Dev'n
Methyl Chloride	416.3	65.8	14.62	1	14.32	67.5	+ 1.7	+ 2.6
Ethyl Chloride	460.4	52.0	19.52	2	19.24	52.9	+ 0.9	+ 1.7
Propyl Chloride	503.2	45.2	23.86	3	24.16	44.5	- 0.7	- 1.6

The value of the exponent "a" for this series is 0.80

Experimental values of T_c/P_c^a versus n for the Chlorine-substituted Paraffins are plotted on Figure 17 from which:

T_c/P_c^a at n = 0 = H + Cl = 9.4 Hence Cl = 7.45

TABLE XXXIII

Critical Pressures of the Alcohols

Compound	Exp'l T_c	Exp'l P_c	Exp'l T_c/P_c^a	n	Calc'd T_c/P_c^a	Calc'd P_c	Dev'n	% Dev'n
Methyl Alcohol	513.2	78.7	30.05	1	29.97	79.0	+ 0.3	+ 0.4
Ethyl Alcohol	516.2	63.1	34.89	2	34.89	63.0	- 0.1	- 0.2
Propyl Alcohol	539.9	49.9	42.28	3	39.81	54.8	+ 4.9	+ 9.8
Butyl Alcohol	560.2	48.4	45.00	4	44.73	48.9	+ 0.5	+ 1.0
Isopropyl Alcohol	508.2	53.0	38.49	3	39.81	50.2	- 2.8	- 5.3
Isobutyl Alcohol	538.2	48.0	43.45	4	44.73	46.0	- 2.0	- 4.2

The value of the exponent "a" for this series is 0.65

Experimental values of T_c/P_c^a versus n for the Alcohols are plotted on Figure 19 from which:

T_c/P_c^a at n = 0 = (OH) + H = 25.1 Hence <u>(OH) = 23.1</u>

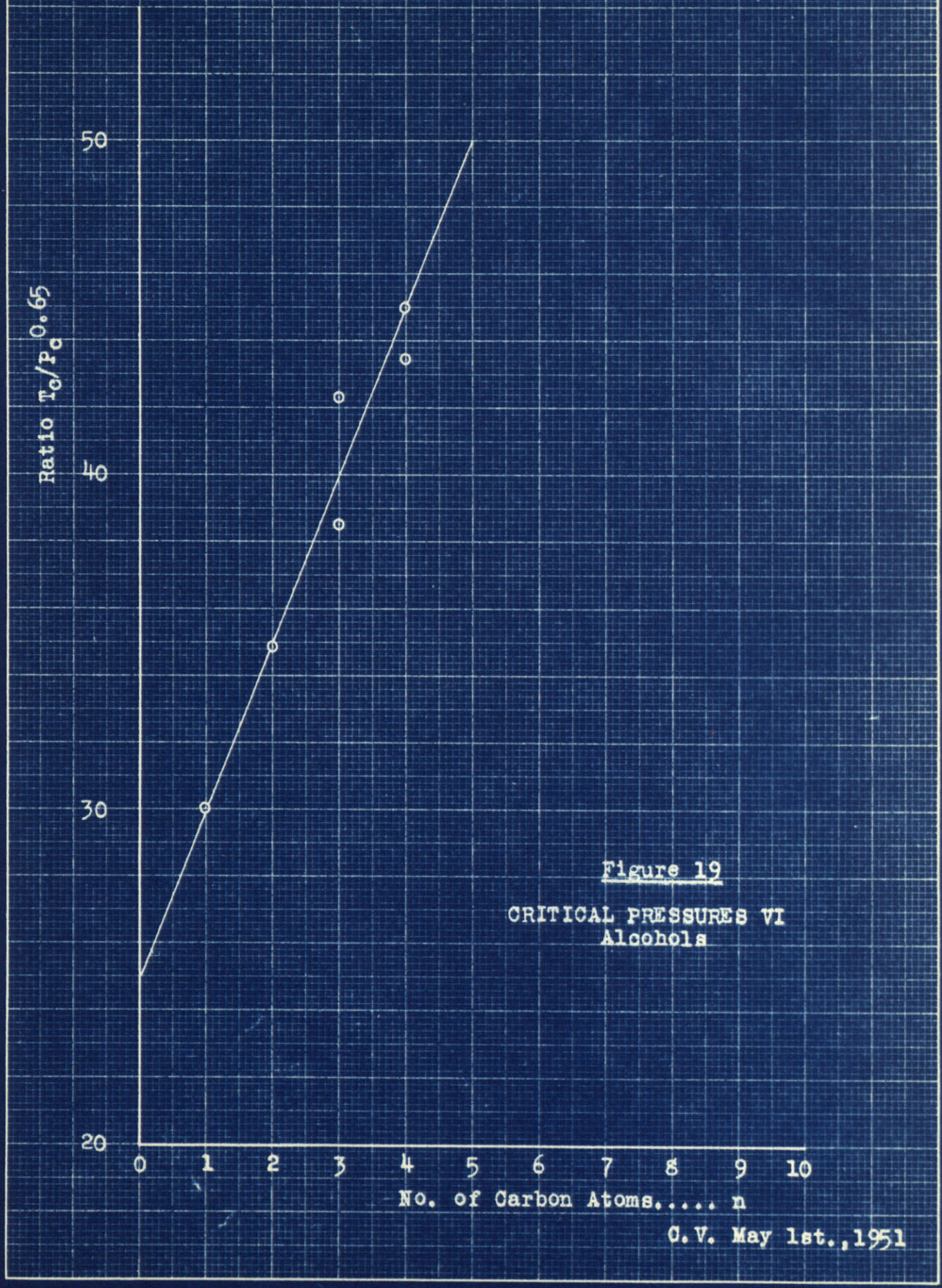

Figure 19

CRITICAL PRESSURES VI
Alcohols

C.V. May 1st., 1951

TABLE XXXIV

Critical Pressures of the Nitriles

Compound	Exp'l T_c	Exp'l P_c	Exp'l T_c/P_c^a	n	Calc'd T_c/P_c^a	Calc'd P_c	Dev'n	% Dev'n
Acetonitrile	547.9	47.7	39.57	2	39.44	48.0	+ 0.3	+ 0.6
Propionitrile	564.4	41.3	44.94	3	44.36	42.2	+ 0.9	+ 2.2
Butyronitrile	582.2	37.4	49.60	4	49.28	37.7	+ 0.3	+ 0.8
Capronitrile	622.2	32.2	58.68	6	59.12	31.9	- 0.3	- 0.9
Benzonitrile	699.2	41.6	-	-	55.80	41.1	- 0.5	- 1.2

The value of the exponent "a" for this series is 0.68

Experimental values of T_c/P_c^a versus n for the Nitriles are plotted on Figure 20 from which:

T_c/P_c^a at n = 0 $= N + T_{cn} - H = 29.6$ Hence $\underline{T_{cn} = 29.1}$

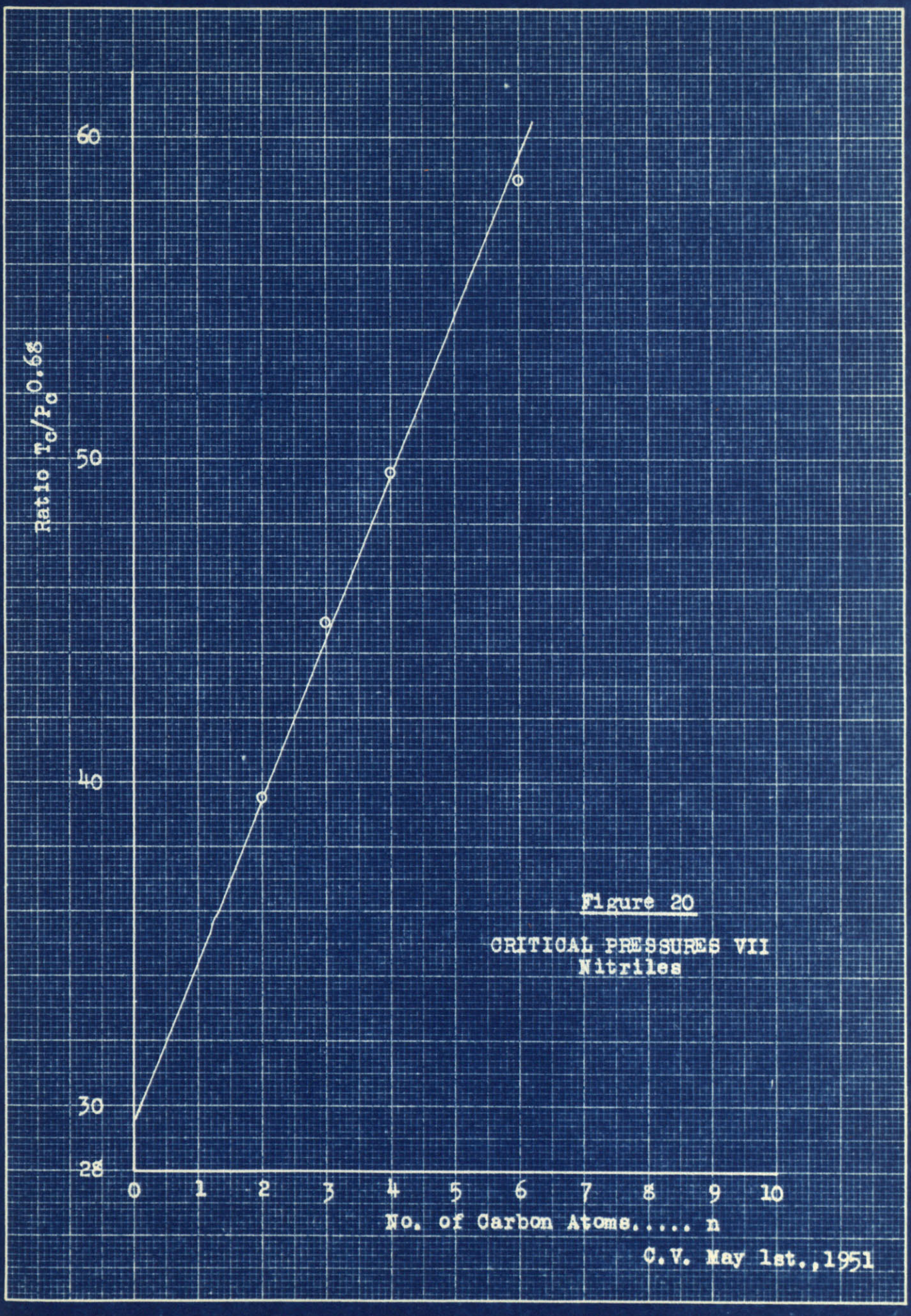

Figure 20

CRITICAL PRESSURES VII
Nitriles

C.V. May 1st., 1951

TABLE XXXV

Critical Pressures of the Phenols

Compound	Calc'd T_c/P_c^a	Exp'l T_c	Exp'l P_c	Calc'd P_c	Dev'n	% Dev'n
Phenol	46.33	692.2	60.5	58.5	- 2.0	- 3.3
o-Cresol	51.25	695.2	49.4	50.6	+ 1.2	+ 2.4
m-Cresol	51.25	705.2	45.0	51.5	+ 6.5	+14.4
p-Cresol	51.25	699.2	50.8	51.0	+ 0.2	+ 0.4

The value of the exponent "a" for this series is 0.665

TABLE XXXVI

Critical Pressures of the Carboxylic Acids

Compound	Calc'd T_c/P_c^a	Exp'l T_c	Exp'l P_c	Calc'd P_c	Dev'n	% Dev'n
Acetic Acid	36.49	594.8	57.2	58.8	+ 1.6	+ 2.8
Propionic Acid	41.41	611.7	53.0	51.0	- 2.0	- 3.8

The value of the exponent "a" for this series is 0.685

Values for remaining Atoms and Structural Elements.

Fluorine

Compound	Exp'l T_c	Exp'l P_c	Exp'l T_c/P_c^a	Calc'd F
Methyl Fluoride	318.1	62.0	11.71	4.84
Dichlorodifluoromethane	384.7	39.6	20.29	2.19
Fluorobenzene	559.2	44.6	26.80	3.57
Fluorine	118.2	25.0	9.00	4.50

The exponent "a" used above is 0.80 and the average value of F = 3.63

Bromine

Compound	Exp'l T_c	Exp'l P_c	Exp'l T_c/P_c^a	Calc'd Br
Bromobenzene	670.2	44.6	32.18	8.95
Hydrogen Bromide	363.2	84.0	11.75	9.80

The exponent "a" used above is 0.80 and the average value of Br = 9.38

Iodine

Compound	Exp'l T_c	Exp'l P_c	Exp'l T_c/P_c^a	Calc'd I
Iodobenzene	721.2	44.6	34.6	11.37
Hydrogen Iodide	424.2	82.0	12.47	10.52

The value of the exponent "a" used is 0.80 and the average value of I = 10.95

Acetylenes

Experimental values are available only for acetylene:

T_c = 312.9°K and P_c = 62.0 atmos.

Hence $T_c/P_c^{0.8}$ = 11.53 and T_{cc} = 5.59

Nitrogen

The experimental values for nitrogen are:

T_c = 126.1°K and P_c = 33.5 atmos.

Hence $T_c/P_c^{0.8}$ = 7.58 and T_{nn} = 2.68

TABLE XXXVII

Critical Pressures of remaining Hydrocarbons and Halogen-substituted Hydrocarbons

Compound	Calc'd T_c/P_c^a	Exp'l T_c	Exp'l P_c	Calc'd P_c	Dev'n	% Dev'n
2-Methyl Propane	23.58	406.9	37.0	35.2	- 1.8	- 4.9
2-Methyl Butane	28.50	461.0	32.9	32.5	- 0.4	- 1.2
3-Methyl Pentane	33.42	500.2	31.9	29.4	- 2.5	- 7.8
2,3-Dimethyl Butane	33.42	500.1	30.7	29.4	- 1.3	- 4.4
2-Methyl Hexane	38.34	531.1	27.2	26.7	- 0.5	- 1.8
3-Methyl Hexane	38.34	535.6	28.1	27.0	- 1.1	- 3.9
2,2-Dimethyl Pentane	38.34	520.9	28.4	26.1	- 2.3	- 8.1
2,3-Dimethyl Pentane	38.34	537.8	29.2	27.1	- 2.1	- 7.2
2,4-Dimethyl Pentane	38.34	520.3	27.4	26.1	- 1.3	- 4.7
2,2,3-Trimethyl Pentane	38.34	531.5	29.7	26.3	- 3.0	-10.1
3-Ethyl Pentane	38.34	540.8	28.6	27.3	- 1.3	- 4.5
2,5-Dimethyl Hexane	43.26	550.0	24.0	24.0	0.0	0.0
2,2,3,3-Trimethyl Butane	43.26	544.0	24.5	23.7	- 0.8	- 3.3
Decane	53.10	603.6	21.3	20.9	- 0.4	- 1.9
Carbon Tetrachloride	30.82	556.3	45.0	37.2	- 7.8	-17.3
Chlorobenzene	30.68	632.2	44.6	43.9	- 0.7	- 1.6
Methyl Fluoride	10.50	318.1	62.0	70.5	+ 8.5	-13.7
Dichlorodifluoro-methane	23.18	384.7	39.6	37.0	- 2.6	- 6.6
Fluorobenzene	26.84	559.2	44.6	44.4	- 0.2	- 0.4
Bromobenzene	32.61	670.2	44.6	43.8	- 0.8	- 1.8
Iodobenzene	34.18	721.2	44.6	45.3	+ 0.7	+ 1.6

The value of the exponent "a" used for the above table is 0.80.

TABLE XXXVIII

Critical Pressures of Elements and Inorganic Compounds

Substance	Calc'd T_c/P_c^a	Exp'l T_c	Exp'l P_c	Calc'd P_c	Dev'n	% Dev'n
Ammonia	8.30	405.6	111.5	129.0	+16.5	+14.8
Carbon Dioxide	12.02	304.3	73.0	57.0	-16.0	-21.9
Carbon Disulfide	19.42	546.2	76.0	65.0	-11.0	-14.5
Fluorine	7.26	118.2	25.0	35.5	+10.5	+42.0
Chlorine	14.90	417.2	76.1	64.5	-11.6	-15.2
Hydrogen chloride	9.40	324.6	81.6	84.0	+ 2.4	+ 2.9
Hydrogen bromide	11.33	363.2	84.0	76.0	- 8.0	- 9.5
Hydrogen iodide	12.90	424.2	82.0	78.5	- 3.5	- 4.3
Hydrogen sulfide	8.65	373.6	88.9	111.0	+22.1	+24.9
Water Vapor	6.90	647.2	217.7	291.0	+73.3	+33.7
Oxygen	8.50	154.4	49.7	37.6	-12.1	-24.4
Hydrogen	3.90	33.1	12.8	14.5	+ 1.7	+13.3
Sulfur Dioxide	15.20	430.4	77.7	65.6	-12.1	-15.6

The exponent "a" used in the above table is 0.80.

TABLE XXXIX

List of Atomic and Structural Values

--- Critical Pressures

Atomic or Structural Element	Symbol	Value
Carbon	C	1.02
Hydrogen	H	1.95
Hydroxyl Group	(OH)	23.10
Oxygen	O	3.00
Nitrogen	N	2.45
Sulfur	S	6.70
Fluorine	F	3.63
Chlorine	Cl	7.45
Bromine	Br	9.38
Iodine	I	10.95
Double Bond (C=C)	D_{cc}	2.50
Double Bond (C=O)	D_{co}	2.50
Double Bond (C=S)	D_{cs}	2.50
Double Bond (S=O)	D_{so}	2.50
Triple Bond (C≡C)	T_{cc}	5.59
Triple Bond (C≡N)	T_{cn}	29.10
Triple Bond (N≡N)	T_{nn}	2.68
Six-membered ring (Aromatic and Naphthenic	R_6	-0.14

DISCUSSION OF RESULTS

V DISCUSSION OF RESULTS

The proposal, that the critical constants of a substance may be predicted by addition of the elemental values of the atoms and structural elements comprising the molecule, is well justified for the critical temperatures and volumes of the different homologous series of organic compounds considered. Out of over sixty compounds the maximum error in the predicted critical volume is 6.95 per cent of the experimental value and ninety per cent of the cases lie within four per cent. Even better agreement is obtained for critical temperatures and for 120 compounds, almost ninety-five per cent of the predicted values lie within three per cent of the experimental, the maximum error encountered being 5.5 per cent. For these cases the average of the deviations from the experimental value for the critical volume case is 1.50 per cent and for the critical temperature case is 1.10 per cent.

Though predicted values of critical temperature are reasonably good for nineteen inorganic compounds, a maximum error of 7.4 per cent being encountered, they are not good for critical volumes and errors up to twenty per cent are met. There appears to be a very good reason for this. In the derivation of the values for the atomic and structural elements, single bond values in all cases have been completely ignored. Consider, however, the paraffin hydrocarbons and assume that the single bonds do in fact have values.

Let S_{cc} be the carbon to carbon single bond value

S_{ch} be the hydrogen to carbon single bond value.

Thus the molecule contains n carbon atoms, (2n + 2) hydroben atoms, (n - 1) carbon to carbon single bonds and (2n + 2) carbon to hydrogen single bonds. The critical volume would thus be:

$$V_c = n\,C + (2n + 2)H + (n - 1)S_{cc} + (2n + 2)S_{ch}$$

$$= n(C + 2H + S_{cc} + 2S_{ch}) + 2H + 2S_{ch} - S_{cc}$$

It is seen that a linear plot of V_c versus n is consistent with this proposition. If similar expressions are derived for other series, a linear relationship between V_c and n is always predicted of slope $(C + 2H + S_{cc} + 2S_{ch})$.

e.g. for the ethers:

$$V_c = n(C + 2H + S_{cc} + 2S_{ch}) + 2H + O + 2S_{ch} - 2S_{cc} + 2S_{co}$$

and for the esters:

$$V_c = n(C + 2H + S_{cc} + 2S_{ch}) + D_{co} + 2 \times O + 2S_{co} - 2S_{cc}$$

where S_{co} represents a carbon to oxygen single bond.

This means that the values obtained herein for the various atomic and structural elements are apparent ones only and that they all contain in some measure parts of single bond values. Unfortunately, it has been impossible so far to devise a method for evaluating the single bond values since always there are two unknowns more than the equations available.

For organic compounds, however, it is clear that compensation for this in the repeating part of the calculated

value, that is, in the ($C + 2H + S_{cc} + 2S_{ch}$) part of it, is inherent in the method of evaluation. Furthermore, with any of the atomic and structural values obtained, there are always associated the same number of single bonds, S_{cx}, where S_{cx} represents the single bond between carbon and X. It is thus only necessary for these to be of equal value to make the method quite applicable despite the use of apparent values. Though it is not possible to say with certainty that this is the case, there are several indications that it is so:

(a) The double bond values obtained in all cases have been in close agreement with one another, e.g. for olefins and diolefins the same value was obtained for the carbon to carbon double bond and furthermore this was equal to or very close to the carbon to oxygen double bond value.

(b) The triple bond values for the critical temperature case closely approached one another.

(c) The six-membered ring value calculated for the aromatics gave good predictions when used for a naphthenic compound, e.g. cyclohexane

The conclusion is that either the single bond values between carbon and another element are nearly equal or else negligible and that the apparent values obtained in this work may be used to calculate the critical volumes and temperatures of organic compounds. However, further work in this field

may reveal a method of obtaining these single bond values.

The reasoning makes it clear that where functional groups are involved such as the hydroxyl group, a value should be assigned to the group as a whole, e.g. the hydroxyl group should properly be assigned a value (OH) and should not be considered as the sum of (O + H).

In view of the above remarks, it becomes clear that good predictions may not be expected generally in the field of inorganic compounds. Here the numbers of the single bonds associated with an already obtained structural value bear no relationship to those above and good predictions may not be expected. For instance, consider hydrogen chloride: this contains a unique hydrogen to chlorine single bond. Similarly, hydrogen gas contains a hydrogen to hydrogen single bond and oxygen gas, an oxygen to oxygen double bond, these structural elements appearing in no other substances.

The predictions of critical temperatures for inorganic compounds are good, the maximum error for nineteen compounds being 7.4 per cent and the average 3.3 per cent. This indicates that the single bond values have no pronounced effects of their own though the somewhat poorer predictions for these cases than for the organic compounds would suggest a slight effect even here. Critical volume predictions for inorganic compounds are erratic, errors as great as twenty per cent being experienced. The average error for twelve

such cases considered is almost nine per cent. On the basis of experience, therefore, reasonable predictions of critical temperature may be anticipated but extreme caution should be used in predicting critical volumes of inorganic compounds.

Serious discrepancy from the straight-line law occurred in only one instance in the case of the critical temperatures of the alcohols. No reason can be suggested to account for this.

The above discussion on single bond values applies equally to the critical pressure case. Discrepancies encountered here are greater than in the critical volume and critical temperature cases, only eighty per cent of the predicted values lying within five per cent of the experimental and ninety-five per cent within ten per cent of these values. These data involve one hundred organic compounds.

The necessity of introducing an exponent on to the critical pressure term which varies in four out of the twelve homologous series considered makes the method of less general application, it being necessary to know the exponent for a series before a prediction may be made. Within the limits of a particular series, however, good predictions are made.

Due to lack of data for compounds having more than eight carbon atoms, except for critical temperatures of nonane and decane and data on several aromatics, the proposed method could not be checked beyond this range but considering the accuracy of prediction up to this point, it seems reasonable

to assume that it may be used considerably beyond it.

The accuracy of prediction in the cases of critical volume and critical temperature is better than that of any other proposed correlation.(see Appendix C) and furthermore the method is of far more general application. Critical pressures are not predicted well by any method so far available and the proposal contained herein is quite as good as any other.

Values have been obtained for relatively few of the atoms and this appears to restrict the application of the method. It may be pointed out, however, that those compounds in the range covered are the ones most generally met with. Extension to other series and to larger molecules is possible as further experimental data become available.

CONCLUSIONS

VI CONCLUSIONS

For organic compounds, critical volumes and critical temperatures may be predicted by the addition of the elemental values of the atoms and structural elements of the molecule. The deviation to be expected for molecules containing eight or less carbon atoms will generally be considerably less than three per cent of the experimental value for critical temperatures and five per cent for critical volumes. Beyond this range, except in a few cases, lack of data prevents the testing of the method. For critical temperatures, this method may be extended to include inorganic compounds though the predictions for these can not be expected to be closer than five per cent generally.

Critical pressures may be predicted by the same technique, though the necessary inclusion of an exponent "a" on the critical pressure term which does vary for some series makes it necessary to know the exponent for the series of which the compound concerned is a member. When this is known, accuracy to within ten per cent of the experimentally determined value may be expected. The method may not be applied to inorganic compounds.

RECOMMENDATIONS

VII RECOMMENDATIONS

A knowledge of the single bond values would make the extension of the method to inorganic compounds generally possible for both critical temperatures and critical volumes.

The inclusion of the exponent "a" on the critical pressure term is undesirable and it may be that another form can be found not requiring such a constant.

Further work along these lines is recommended.

APPENDIX

APPENDIX A: DEFINITIONS AND EXPERIMENTAL DETERMINATION OF CRITICAL CONSTANTS

If the temperature of a substance is raised from a temperature at which it is liquifiable by the application of pressure isothermally, then a temperature, unique for each substance, is reached eventually at which and above which isothermal pressure application will no longer liquify it no matter how high the applied pressure. This temperature is called the Critical Temperature of the substance. As the temperature is raised towards the critical, the density of the liquid phase decreases and that of the saturated vapor phase increases until at the critical the meniscus separating the two phases disappears and they become identical. The pressure corresponding to the saturated vapor pressure at the critical temperature is called the Critical Pressure and the density of the substance at this point, the Critical Density. The Molal Critical Volume is the molecular weight of the substance divided by the critical density.

Methods of Determining the Critical Constants.

(1) The substance to be considered is placed in a sealed glass tube (laboratory tube) and the temperature is raised gradually until the meniscus separating the two phases just disappears. At this point, the temperature is noted and then, after raising it somewhat, is allowed to fall gradually. When the meniscus re-appears, the temperature is again noted. The mean of the two observed temperatures obtained is taken as the critical.

This method is not considered very accurate since small quantities of impurity present in the substance retard the equilibrium.

(2) If a laboratory tube is connected to a suitable manometer and means provided for varying the pressure, then for a substance under investigation a temperature can be found at which a slight decrease in pressure will cause a temporary re-appearance of the meniscus until the temperature re-establishes itself. This temperature is taken as the critical. The pressure measured at this point is taken as the critical pressure. Most observers use this technique.

(3) The critical density is very difficult to determine accurately by measurement because of the extreme compressibility of substances at the critical point. In addition, it is found that the density at the critical point varies considerably at different vertical levels due to hydrostatic head. For instance, it is found that in a tube containing carbon dioxide at the critical point, the difference between the densities at two points ten centimeters apart vertically is of the order of 6 per cent.

The best method devised for its measurement is that by Cailletet and Mathias (8) who discovered that if the densities of the liquid and vapor phases at different temperatures extending almost up to the critical point are plotted against the corresponding temperatures, then the locus of the 'means" of these densities is a straight line for most substances. This they called the Rectilinear Diameter. The equation of this line can be obtained in terms of temperature and if the critical temperature is inserted in this equation, then the critical density is given.

For some substances, especially those with a high critical temperature, the rectilinear diameter is found to be slightly curved but in most cases it may be considered to be straight.

APPENDIX B: LIST OF EXPERIMENTALLY DETERMINED CRITICAL CONSTANTS

(1) Paraffin Hydrocarbons

Compound	P_c atmos.	T_c °K	V_c ccs/grm mol
Methane	45.8 (55)	190.7 (55)	97.8 (55)
Ethane	48.8 (55)	305.3 (27)	142.9 (55)
Propane	42.0 (2)	370.2 (27)	194.7 (2)
Butane	37.47 (3)	425.2 (3)	266.6 (3)
2-Methylpropane	37.0 (55)	406.9 (27)	
Pentane	33.0 (70)	470.5 (70)	318.9 (70)
2-Methylbutane	32.9 (70)	461.0 (70)	308.0 (70)
Hexane	30.0 (70)	-	366.9 (70)
2-Methylpentane	-	501.2 (50)	-
3-Methylpentane	31.9 (50)	500.2 (50)	-
2,3-Dimethylbutane	30.7 (70)	-	357.0 (70)
Heptane	27.6 (15)	542.7 (15)	-
2-Methylhexane	27.2 (15)	531.1 (15)	-
3-Methylhexane	28.1 (15)	535.6 (15)	-
2,2-Dimethylpentane	28.4 (15)	520.9 (15)	-
2,3-Dimethylpentane	29.2 (15)	537.8 (15)	-
2,4-Dimethylpentane	27.4 (15)	520.3 (15)	-
2,2,3-Trimethylbutane	29.7 (15)	531.5 (15)	-
3-Ethylpentane	28.6 (15)	540.8 (15)	-
Octane	25.2 (70)	-	489.9 (70)
2,5-Dimethylhexane	24.05 (70)	550.0 (70)	482.0 (70)
2,2,3,3-Trimethylbutane	24.5 (33)	544.0 (33)	482.0 (33)
Nonane	-	596.0 (56)	-
Decane	21.3 (1)	603.6 (1)	-

(2) Olefins

Compound	P_c atmos.	T_c °K	V_c ccs/grm mol
Ethylene	50.9 (55)	283.1 (10)	127.2 (55)
Propylene	45.0 (55)	365.3 (10)	-
Butene-1	-	417.2 (10)	-
2-Methylpropene	-	423.9 (41)	-
Pentene-1	40.4 (33)	474.4 (41)	-
3-Methylbutene-1	33.9 (48)	464.8 (41)	-
2-Methylbutene-2	-	464.8 (50)	-
Hexene-1	-	516.7 (1)	-
Hexene-1	-	517.0 (50)	-
Octene-1	-	578.0 (41)	-

(3) Diolefins

Compound	P_c atmos.	T_c °K	V_c ccs/grm mol
Propadiene	-	393.9 (4)	-
Butadiene-1,3	42.7 (54)	425.2 (54)	220.5 (54)
Hexadiene-1,5	-	507.6 (41)	-

(4) Acetylenes

Compound	P_c atmos.	T_c °K	V_c ccs/grm mol
Acetylene	62.0 (55)	312.9 (45)	112.7 (55)
Methyl Acetylene	-	394.8 (45)	-
Ethyl Acetylene	-	463.7 (45)	-
Dimethyl Acetylene	-	488.7 (46)	-
Propyl Acetylene	-	493.5 (46)	-

(5) Aromatics

Compound	P_c atmos.	T_c °K	V_c ccs/grm mol
Benzene	47.9 (70)	561.7 (70)	256.2 (70)
Toluene	41.6 (1)	593.8 (41)	315.1 (34)
o-Xylene	36.9 (1)	631.5 (1)	-
m-Xylene	35.8 (1)	618.8 (1)	-
p-Xylene	35.0 (1)	617.6 (1)	-
Ethyl Benzene	38.1 (1)	619.2 (56)	-
1,2,4-Trimethyl Benzene	33.2 (1)	654.4 (1)	-
1,3,5-Trimethyl Benzene	33.2 (1)	640.2 (56)	-
Propyl Benzene	32.3 (1)	638.8 (1)	-
Isopropyl Benzene	32.2 (1)	635.9 (56)	-
1-Methyl-2-isopropyl Benzene	28.6 (1)	651.8 (1)	-
1-Methyl-4-isopropyl Benzene	28.6 (1)	651.8 (1)	-
1,2,3,5-Tetramethyl Benzene	-	662.2 (56)	-
1,2,4,5-Tetramethyl Benzene	28.6 (25)	675.7 (25)	-

Aromatics (con't)

Compound	P_c atmos.	T_c °K	V_c ccs/grm mol
Isobutyl Benzene	31.1 (21)	650.2 (56)	-
Pentamethyl Benzene	-	691.2 (56)	-
Isoamyl Benzene	-	655.2 (56)	-

(6) Remaining Hydrocarbons

Compound	P_c atmos.	T_c °K	V_c ccs/grm mol
Cyclohexane	39.8 (70)	555.0 (42)	308.0 (70)
Methyl cyclohexane	-	580.0 (42)	-
Cyclopropane	54.0 (42)	398.0 (42)	-
Biphenyl	41.4 (11)	801.2 (11)	448.9 (11)
Biphenyl Methane	28.2 (25)	802.2 (64)	-
1,2-Biphenyl Ethane	-	765.2 (64)	-
Naphthalene	39.2 (25)	749.7 (9)	-
Acenaphthene	-	803.2 (64)	-

(7) Alcohols

Compound	P_c atmos.	T_c °K	V_c ccs/grm mol
Methyl Alcohol	78.7 (32)	513.2 (32)	117.7 (32)
Ethyl Alcohol	63.1 (32)	516.3 (32)	167.3 (32)
n-Propyl Alcohol	49.9 (32)	536.9 (32)	219.8 (32)
Isopropyl Alcohol	53.0 (48)	508.2 (48)	-
n-Butyl Alcohol	48.4 (32)	560.2 (32)	-
Isobutyl Alcohol	48.0 (48)	538.2 (48)	-
sec-Butyl Alcohol	-	538.2 (7)	-
tert-Butyl Alcohol	-	508.2 (52)	-
Isoamyl Alcohol	-	580.2 (52)	-
tert-Amyl Alcohol	-	545.2 (7)	-
n-Heptyl Alcohol	-	638.2 (7)	-
n-Octyl Alcohol	-	658.2 (7)	-
sec-Octyl Alcohol	-	637.2 (7)	-
Allyl Alcohol	-	545.2 (48)	-

(8) Ethers

Compound	P_c atmos.	T_c °K	V_c ccs/grm mol
Methyl Ether	52.0 (32)	400.1 (32)	169.7 (32)
Methyl Ethyl Ether	43.4 (6)	437.9 (6)	222.2 (6)
Ethyl Ether	35.5 (32)	467.0 (32)	282.4 (32)
Ethyl Propyl Ether	32.1 (6)	500.6 (6)	341.1 (6)
Ethyl Allyl Ether	-	518.2 (52)	-
Methylene Diethyl Ether	-	527.2 (52)	-

(9) Carboxylic Acids and Esters

Compound	P_c atmos.	T_c °K	V_c ccs/grm mol
Methyl Formate	59.1 (32)	487.2 (32)	171.9 (32)
Ethyl Formate	46.6 (70)	508.5 (72)	229.1 (70)
Propyl Formate	40.1 (32)	538.0 (32)	284.8 (32)
Isobutyl Formate	38.0 (49)	551.2 (49)	354.2 (49)
Isoamyl Formate	34.0 (49)	576.2 (49)	411.4 (49)
Acetic Acid	57.2 (32)	594.8 (32)	170.9 (32)
Methyl Acetate	46.3 (32)	506.9 (32)	227.7 (32)
Ethyl Acetate	37.8 (32)	523.2 (32)	285.7 (32)
Propyl Acetate	32.9 (32)	549.4 (32)	344.6 (32)
n-Butyl Acetate	-	579.2 (53)	-
Isobutyl Acetate	31.0 (49)	561.2 (49)	415.8 (49)
Isoamyl Acetate	-	599.2 (7)	-
Propionic Acid	53.0 (32)	611.7 (32)	234.9 (32)
Methyl Propionate	39.3 (32)	530.6 (32)	282.1 (32)
Ethyl Propionate	33.0 (32)	546.1 (32)	344.6 (32)
Propyl Propionate	-	578.2 (53)	-
Isobutyl Propionate	-	592.2 (53)	-
Isoamyl Propionate	-	611.2 (7)	-
n-Butyric Acid	-	628.2 (32)	291.4 (32)
Isobutyric Acid	-	609.2 (32)	290.0 (32)
Methyl Butyrate	34.2 (32)	554.5 (32)	340.0 (32)
Methyl Isobutyrate	33.7 (32)	540.7 (32)	339.0 (32)
Ethyl Butyrate	30.0 (49)	566.2 (49)	405.8 (49)
Ethyl Isobutyrate	30.0 (49)	553.2 (49)	420.0 (49)
Propyl Butyrate	-	600.2 (53)	-
Propyl Isobutyrate	-	589.2 (53)	-
Isobutyl Isobutyrate	-	602.2 (7)	-
Isoamyl Isobutyrate	-	619.2 (7)	-
n-Valeric Acid	-	652.2 (7)	-
Isovaleric Acid	-	634.2 (7)	-

Carboxylic Acids and Esters (cont)

Compound	P_c atmos.	T_c °K	V_c ccs/grm mol
Methyl Valerate	32.0 (32)	567.2 (32)	- (32)
Ethyl Valerate	-	570.2 (13)	-
Ethyl Isovalerate	-	588.2 (7)	-
Propyl Isovalerate	-	609.2 (7)	-
Isobutyl Isovalerate	-	621.2 (7)	-
Ethyl Caprylate	-	659.2 (7)	-
Ethyl Nonylate	-	673.2 (7)	-

(10) Amines

Compound	P_c atmos.	T_c °K	V_c ccs/grm mol
Methylamine	73.6 (5)	430.1 (5)	-
Ethylamine	55.5 (5)	456.4 (5)	-
Propylamine	46.3 (5)	497.0 (5)	-
Dimethylamine	51.7 (5)	437.8 (5)	-
Diethylamine	36.2 (32)	496.7 (32)	297.0 (32)
Dipropylamine	31.0 (63)	550.2 (63)	-
Trimethylamine	41.0 (63)	434.2 (63)	-
Triethylamine	30.0 (32)	535.2 (32)	402.0 (32)
Aniline	52.4 (26)	699.2 (26)	-
Methyl Aniline	51.3 (32)	702.2 (32)	-
Dimethyl Aniline	35.8 (26)	688.2 (26)	-

(11) Nitriles

Compound	P_c atmos.	T_c °K	V_c ccs/grm mol
Acetonitrile	47.7 (32)	547.9 (32)	171.0 (32)
Propionitrile	41.3 (60)	564.4 (60)	228.5 (60)
Butyronitrile	37.4 (26)	582.2 (26)	-
Capronitrile	32.2 (26)	622.2 (26)	-
Benzonitrile	41.6 (26)	699.2 (26)	-
Tolunitrile	-	723.2 (32)	-

(12) Mercaptans and Sulfides

Compound	P_c atmos.	T_c °K	V_c ccs/grm mol
Methyl Mercaptan	71.4 (6)	470.0 (6)	148.8 (6)
Ethyl Mercaptan	54.2 (6)	498.7 (6)	206.0 (6)
Isoamyl Mercaptan	-	594.2 (20)	-
Methyl Sulfide	54.6 (6)	503.1 (6)	203.0 (6)
Methyl Ethyl Sulfide	42.0 (62)	533.2 (62)	-
Ethyl Sulfide	39.1 (6)	557.0 (6)	323.0 (6)
Isoamyl Sulfide	-	664.2 (20)	-
Ethyl Disulfide	-	642.2 (20)	-
Allyl Sulfide	-	653.2 (20)	-
Thiophene	48.0 (52)	590.2 (52)	-

(13) Halogen-substituted Hydrocarbons

Compound	P_c atmos.	T_c °K	V_c ccs/grm mol
Carbon Tetrachloride	45.0 (32)	556.3 (32)	276.0 (32)
Chloroform	-	536.2 (32)	231.0 (32)
Methyl Chloride	65.8 (55)	416.3 (55)	136.5 (55)
Ethyl Chloride	52.0 (55)	460.4 (55)	195.5 (55)
n-Propyl Chloride	45.2 (32)	503.2 (32)	-
Chlorobenzene	44.6 (32)	632.2 (32)	308.2 (32)
Ethyl Bromide	-	504.2 (32)	212.3 (32)
Bromobenzene	44.6 (32)	670.2 (32)	322.8 (32)
Methyl Fluoride	62.0 (32)	318.1 (32)	-
Dichlorodifluoromethane	39.56(54)	384.7 (54)	218.0 (54)
Fluorobenzene	44.6 (32)	559.2 (32)	271.5 (32)
Iodobenzene	44.6 (32)	721.2 (32)	351.1 (32)

(14) Remaining Organic Compounds

Phosgene	56.0 (28)	455.2 (22)	190.6 (51)
Cyanogen	59.0 (55)	401.2 (55)	-
Acetaldehyde	-	461.2 (31)	-
Ethylene Oxide	-	465.2 (39)	-

Remaining Organic Compounds (cont)

Compound	P_c atmos.	T_c °K	V_c ccs/grm mol
Acetone	47.0 (29)	508.2 (29)	216.7 (29)
Methylal	-	497.2 (52)	-
Acetic Anhydride	46.0	569.2 (52)	-
Methyl Oxalate	9.48 (32)	533.2 (32)	-
Pyridine	60.0 (32)	617.2 (32)	-
Phenol	60.5 (32)	692.2 (32)	-
o-Cresol	49.4 (32)	695.2 (32)	-
m-Cresol	45.0 (26)	705.2 (26)	-
p-Cresol	50.8 (32)	699.2 (32)	-
Ethyl Crotonate	-	599.2 (52)	-
Paraldehyde	-	563.2 (31)	-
Anisole	41.3 (26)	642.2 (26)	-
Phenetole	33.8 (26)	647.2 (26)	-
Dimethyl-o-toluidine	30.8 (32)	668.2 (26)	-
Thymol	-	793.2 (32)	-

(15) Elements and Inorganic Compounds

Compound	P_c atmos.	T_c °K	V_c ccs/grm mol
Ammonia	111.5 (55)	405.6 (55)	72.4 (55)
Argon	48.0 (55)	151.2 (55)	150.5 (55)
Arsenic	342.0 (54)	1076.2 (54)	-
Boron Tribromide	-	573.2 (54)	278.5 (54)
Bromine	-	575.2 (54)	-
Carbon Dioxide	73.0 (55)	304.3 (55)	95.7 (55)
Carbon Disulfide	76.0 (32)	546.2 (32)	172.5 (32)
Carbon Monoxide	35.0 (55)	134.2 (55)	90.1 (55)
Carbon Oxysulfide	61.0 (32)	378.2 (32)	-
Chlorine	76.1 (55)	417.2 (55)	124.0 (55)
Cyanogen	59.0 (55)	401.2 (55)	-
Fluorine	25.0 (54)	118.2 (54)	-
Germanium Tetrachloride	38.0 (32)	550.2 (32)	-
Helium	2.26 (55)	5.30 (55)	115.6 (55)
Hydrazine	145.0 (32)	653.2 (32)	-
Hydrogen	12.8 (55)	33.1 (55)	64.5 (55)
Hydrogen Bromide	84.0 (55)	363.2 (55)	-
Hydrogen Chloride	81.6 (55)	324.6 (55)	87.0 (55)
Hydrogen Cyanide	50.0 (32)	456.7 (32)	135.0 (32)
Hydrogen Fluoride	-	503.4 (54)	-
Hydrogen Iodide	82.0 (55)	424.2 (55)	-
Hydrogen Selenide	88.0 (32)	411.2 (32)	-
Hydrogen Sulfide	88.9 (55)	373.6 (55)	-

Elements and Inorganic Compounds (cont)

Compound	P_c atmos.	T_c °K	V_c ccs/grm mol
Iodine	-	826.2 (32)	-
Krypton	54.0 (55)	210.2 (55)	227.5 (55)
Neon	25.9 (55)	44.1 (55)	83.4 (55)
Niton	62.5 (54)	377.7 (54)	-
Nitric Oxide	65.0 (55)	179.2 (55)	57.7 (55)
Nitrogen	33.5 (55)	126.1 (55)	90.0 (55)
Nitrogen Tetroxide	99.0 (32)	431.2 (32)	-
Nitrous Oxide	71.7 (55)	309.7 (55)	97.8 (55)
Oxygen	49.7 (55)	154.4 (55)	74.5 (55)
Radon	62.0 (32)	377.2 (32)	-
Silicon Tetrafluoride	50.0 (32)	271.7 (32)	-
Silicon Tetrahydride	48.0 (32)	269.7 (32)	-
Stannic Tetrachloride	37.0 (32)	591.7 (32)	351.5 (32)
Steam	217.7 (32)	647.2 (32)	45.0 (32)
Sulfur	-	1313.2 (32)	-
Sulfur Dioxide	77.7 (55)	430.4 (55)	123.2 (55)
Sulfur Trioxide	83.6 (32)	491.5 (32)	127.0 (32)
Water	218.4 (32)	647.35 (32)	54.1 (32)
Xenon	58.2 (55)	289.8 (55)	227.5 (55)

APPENDIX C: REVIEW OF EXISTING METHODS FOR PREDICTING CRITICAL CONSTANTS

(1) CRITICAL VOLUMES

Mathias (40) shows that in accordance with the Law of Rectilinear Diameters:

$$D_c = M/V_c = 1/2(D - d)/(2 - T/T_c) \qquad (A1)$$

where D_c = Critical Density (grms/cc)
M = Molecular Weight
V_c = Critical Volume (ccs/grm mol)
D = Saturated Liquid Density at Temperature T°K (grms/cc)
d = Saturated Vapor Density at T°K (grms/cc)
T_c = Critical Temperature (°K)

Table A1 presents the results predicted by this relationship for thirteen compounds chosen at random and calculated by the author. It shows that while good agreement is attained in some instances, not only are large errors frequently involved, but that there is considerable variation in the predicted value depending on the reference temperature chosen.

TABLE A1

Errors involved in applying Equation (A1)

Compound	T	T_c	Calc'd D_c	Exp'l D_c	% Error
Ammonia	239	405.6	0.242	0.235	+ 2.98
	297		0.234		- 0.43
	322		0.228		- 2.98
n-Butane	293	425.2	0.221	0.225	- 1.78
	389		0.175		-22.20
Butadiene-1,3	200	425.2	0.238	0.245	- 2.86
	256		0.238		- 2.86
	311		0.232		- 5.30
Carbon Dioxide	228	304.3	0.446	0.460	- 3.04
Dichlorodifluoromethane	243	384.7	0.542	0.555	- 2.34
	261		0.538		- 3.06
	311		0.508		- 8.47

TABLE A1 (cont)

Compound	T	T_c	Calc'd D_c	Exp'l D_c	% Error
Ethane	150	305.3	0.194	0.210	- 7.81
	222		0.193		- 8.10
	300		0.100		-52.40
Ethylene	178	283.1	0.202	0.220	- 8.19
	211		0.198		-10.25
	256		0.162		-26.20
Methyl Chloride	250	416.3	0.357	0.370	- 3.52
	256		0.357		- 3.52
	350		0.323		-12.70
Methyl Formate	273.2	487.2	0.348	0.349	- 0.29
Nitrogen	77.4	126.1	0.290	0.311	- 6.75
	90.0		0.280		- 9.95
	110.0		0.248		-20.20
Oxygen	90.2	154.4	0.404	0.430	- 6.05
	105		0.397		- 7.67
	120		0.358		-16.75
Propane	211	370.2	0.212	0.226	- 6.20
	250		0.210		- 7.80
	289		0.202		-10.62
Sulfur Dioxide	200	430.4	0.529	0.520	+ 1.73
	300		0.520		0.00

Young (71) suggests the relationship:

$$D_c = 3.7\ MP_c/RT_c \qquad (A2)$$

where P_c = Critical Pressure (ats)
R = 82.07 cc. ats/°K grm mol.

The results predicted by this proposed formula for sixteen compounds are presented in Table A2 from which it is seen that a reasonable degree of accuracy is attained over a wide range of substances. For the hydrocarbons especially are the predicted values accurate. The obvious disadvantage of course lies in the fact that a knowledge of both critical pressure and temperature are required before a prediction can be made.

TABLE A2

Errors involved in applying Equation (A2)

Compound	Cal'd	Exp'l	% Error
Acetylene	0.233	0.231	+ 0.86
Acetic Acid	0.261	0.351	-25.60
Ammonia	0.211	0.235	-10.20
Benzene	0.304	0.305	- 0.30
Carbon Tetrachloride	0.563	0.520	+ 8.28
Chlorine	0.602	0.573	+ 5.06
Chlorobenzene	0.358	0.365	- 1.92
Dichlorodifluoromethane	0.570	0.555	+ 2.70
Ethane	0.217	0.210	+ 3.34
Ethyl Formate	0.306	0.323	- 5.27
Ethylene	0.228	0.220	+ 3.64
Helium	0.077	0.069	+11.10
Heptane	0.230	0.234	- 1.71
Hydrogen	0.035	0.031	+11.94
Methane	0.174	0.162	+ 7.29
Pentane	0.229	0.232	- 1.30

In almost all the more recent attempts at correlation and prediction of critical volumes, the parachor and molar refraction have been used as parameters.

Sugden (59) was the first to point out that some relationship between the parachor and critical volume may be expected. The basis of this reasoning was that liquid volumes should be compared under equal conditions of internal pressure, and not equal temperature or reduced temperature, since under these conditions intermolecular force field intensities are approximately the same. Internal pressure is closely related to surface tension and since the surface tension of all substances is zero at the critical point, a relationship appeared likely between the parachor and the critical volume. The equation he proposed was:

$$[P] = 0.77\ V_c \qquad \text{(A3)}$$

where $[P]$ = Parachor

From data published subsequently, it appears that the constant varies over the range 0.635 for octadecane to 0.93 for water and thus equation (A3) is not accurate enough for practical purposes.

Meissner and Redding (44) suggested the relationship:

$$V_c = (0.377\ [P] + 11)^{1.25} \qquad (A4)$$

It is stated that V_c may be computed from this equation with considerable accuracy except in the cases of water and biphenyl. It is also pointed out that in the case of simple compounds showing anomalous computed parachor values, the critical volume may be computed with good accuracy if the experimental parachor value is used.

Ferguson (18) by means of a dimensional analysis of the parachor, suggests:

$$[P] = K\ V_c^{5/6}\ T_c^{1/4} \qquad (A5)$$

where $K = 0.41$

but subsequently (19) offered:

$$[P] = K\ V_c^{7/8}\ T_c^{1/4} \qquad (A6)$$

which is not dimensionally consistent but which yields more accurate results.

Lautie (35) offered:

$$[P] = 0.681\ V_c^{3/4}\ T_c^{1/4} \qquad (A7)$$

$$[P] = 0.316\ V_c P_c^{1/4} \qquad (A8)$$

by combination of several theoretical and empirical equations which apply strictly only to normal liquids.

Herzog (30) discussed these equations. Equation (A5) has the most rational basis and, thus, by re-arrangement, may be stated:

$$V_c = K[P]^{1.2}/T_c^{0.3} \qquad (A9)$$

Dividing the data empirically into two groups:

(a) For compounds with functional groups:

-C=O ; -C≡N ; -COOH ; and -OH and one to three additional non-functional carbons:

$$V_c = 3.34[P]^{1.2}/T_c^{0.3} \qquad (A10)$$

The reliability of this equation is 10%, reliability being defined as: $(2s/V_m)100\%$

where V_m = the mean value of the critical volumes of all the compounds considered

$$s = \left\{ \frac{\sum \left[(V_c)\text{calc'd} - (V_c)\text{exp'l} \right]^2}{(n-2)} \right\}^{1/2}$$

n = the number compounds considered

2s = a measure of the deviation to be expected in 95% of the cases.

(b) For all other compounds:

$$V_c = 2.92[P]^{1.2}/T_c^{0.3} \qquad \text{(A11)}$$

The reliability in this case is 6.5%.

Thus it is seen that errors are high and not much influenced by errors in the critical temperature since an error of 5% in this produces an error of less than 2% in the predicted critical volume.

An analysis of Lautie's equation (A8) shows:

On re-arranging $$V_c = K[P]/P_c^{0.25} \qquad \text{(A12)}$$

and empirically separating the data into three groups:

(1) Aliphatic Organic compounds containing two or less carbons in addition to the functional atom or group, (e.g. CH_4 , C_2H_5OH , C_2H_5COOH) and all other compounds having a critical temperature less than 450°K:

$$V_c = 3.58[P]/P_c^{0.25} \qquad \text{(A13)}$$

Reliability = 8.1%

(2) Aliphatic organic compounds containing three or four carbons in addition to the functional atom or group and all other compounds having a critical temperature lying between 450°K and 600°K:

$$V_c = 3.31[P]/P_c^{0.25} \qquad \text{(A14)}$$

Reliability = 5.2%

(3) Aliphatic organic compounds containing more than four carbons in addition to the functional atom or group and all other compounds having a critical temperature greater than 600 K° (excluding water):

$$V_c = 3.19[P]/P_c^{0.25} \qquad (A15)$$

Reliability = 7.5%

Thus, it is seen that there is little to choose between equations (A9) and (A12), but since the critical temperature is both easier to measure and to predict than the critical pressure, equation (A9) is the more useful.

Consideration of the equations of Sugden (59) and of Meissner and Redding (44) on the same basis yields the following results:

$$V_c = 1.447[P] - 20.09 \qquad (A16)$$

Reliability = 18.1%

$$V_c = (0.3591[P] + 14.0)^{1.25} \qquad (A17)$$

Reliability = 15.7%

In equation (A16) the form of Sugden's original equation has been modified slightly in order to better fit the data, and in equation (A17) the constants have been modified slightly since Meissner and Redding used only the data for hydrocarbons whereas equation (A17) includes all the data available.

Further investigation of equations of the form:

$$V_c = (F[P] + G)^n \qquad (A18)$$

for values of n varying from 1.00 to 1.25 indicate that the accuracy of the correlation is not very sensitive to n.

Meissner (43) in a further attempt to correlate the critical volumes of all substances suggests:

$$V_c = 0.55(1.5[P] + 9 - 4.34[R_D])^{1.155} \qquad (A19)$$

where $[R_D]$ = Molar refraction measured with monochromatic light of wavelength corresponding to the Sodium D line.

The largest errors in the hundred compounds tested were with biphenyl and methyl formate, these two substances giving predicted values 10% greater than the experimental values. For many classes of compounds precision is much better than this, e.g. with normal aliphatic hydrocarbons, the maximum error is less than 5%.

Watson (67) shows that for all liquids investigated the compressibility and thermal expansion data can be represented satisfactorily by the relation:

$$V = V_1 \omega_1 / \omega \qquad (A20)$$

where V = Molal volume in ccs. at Reduced Temperature T_r and Reduced Pressure P_r
ω = Expansion Factor at T_r and P_r
ω_1 and V_1 correspond to T_{r1} and P_{r1}

The factor ω is a dimensionless quantity termed the Expansion Factor which, when expressed as a function of P_r and T_r, is approximately the same for all liquids, the deviation from the values of the Molal Volume given by Equation (A20) being generally less than 5%.

At the critical point: $\omega = 0.044$
$V = V_c$

Therefore $$V_c = V_1 \omega_1 / 0.044 \qquad (A21)$$

and thus, if $V_1 \omega_1$ can be predicted, the molal critical volume is given immediately from equation (A21). From a study of various hydrocarbons, it is seen that for:

(a) Paraffins: $$V_1 \omega_1 = 1.88 + 2.44\ n_c \qquad (A22)$$

(b) Mono-olefins: $$V_1 \omega_1 = 1.10 + 2.44\ n_c \qquad (A23)$$

(c) Monocyclic aromatics: $$V_1 \omega_1 = -3.0 + 2.44\ n_c \qquad (A24)$$

For series of polar compounds, the increment in $V_1 \omega_1$ for a CH_2 group tend to vary at lower members and approaches 2.44 for higher molecular weights. The relationship between n_c and $V_1 \omega_1$ may be expressed:

$$V_1 \omega_1 = a + 2.44\ n_c + m \log n_c \qquad (A25)$$

For Alcohols:

$$V_1 \omega_1 = 2.89 + 2.44\ n_c - 1.23 \log n_c \qquad (A26)$$

(2) CRITICAL TEMPERATURE

Since the critical temperature is the limit of the boiling temperature with increasing pressure, it is to be expected that there exists a relationship between the critical and normal boiling temperatures. Guldberg (24) was the first to propose such a relationship and suggested:

$$T_c/T_b = 1.5 \qquad \text{(A27)}$$

where T_c and T_b are the critical and normal boiling temperatures respectively expressed in absolute units. It has been shown experimentally, however, that this ratio varies between the limits of 1.3 and 1.8.

Several modifications of Guldberg's simple rule have been proposed, the best being the "Rule of Three Temperatures" given by Prud'homme (57) which states that:

$$(T_b + T_m)/T_c = \text{Constant} \qquad \text{(A28)}$$

where T_m is the normal melting temperature also expressed in absolute units. Experimentally, the constant in equation (A28) is found to vary between the limits of 1.0 and 1.10.

Meissner and Redding (44) considered the equation:

$$T_c = a\,T_b + c \qquad \text{(A29)}$$

and found that though this expression is not universally true with one set of constants, if all substances are divided up into four groups, then a set of constants can be found for each which satisfy all the substances in that group. It was pointed out that the equations proposed, given below, give a maximum deviation between experimental and computed values of 5%.

(A) Compounds boiling below 234°K:

$$T_c = 1.7\,T_b - 2.0 \qquad \text{(A30)}$$

This relationship applies to all elements regardless of boiling temperature.

(B) Compounds boiling above 235°K:

(a) Compounds containing a halogen or a sulfur:

$$T_c = 1.41\,T_b + 66 - 11\,F \qquad \text{(A31)}$$

where F = the number of fluorine atoms in the molecule.

(b) Aromatics and Naphthenes (halogen and sulfur free):

$$T_c = 1.41\ T_b + 66 - r\ (0.383\ T_b - 96) \qquad (A32)$$

where r = the ratio of the non-cyclic carbon atoms to the total carbon atoms in the molecule.

(c) All other compounds (halogen and sulfur free):

$$T_c = 1.027\ T_b + 159 \qquad (A33)$$

The above equations were not tested above 600°K.

Watson (66) developed a formula for the determination of T_c for non-polar compounds* which states:

$$T_e/T_c = 0.283\ (M/D_s)^{0.18} \qquad (A34)$$

where T_e = Absolute temperature of liquid whose saturated vapor occupies 22.4 liters per grm mol.
T_c = Absolute critical temperature.
M = Molecular weight.
D_s = Density of the liquid at its normal boiling point in grms. per cc.

The temperature T_e is a function of the normal boiling temperature of the substance. A plot of $(T_e - T_b)$ versus T_b is presented on Figure A1.

Watson showed that for 25 non-polar substances with widely varying boiling points, the general difference between T_e/T_c calculated and observed was less than 2%.

The method, where it could be applied, was probably the most accurate known since it is supported by practically all the reliable data for non-polar compounds which would not be expected to be associated or dissociated in either the liquid or the vapor phase. It breaks down for substances with low boiling points, e.g. hydrogen and helium.

* A non-polar compound is one in which the atoms of the molecule are symmetrically arranged so that there are no unbalanced electrical charges. Generally, they are chemically inactive, do not ionise well or conduct electricity. Hydrocarbons of practically all series are relatively non-polar whereas water, alcohol, ammonia, etc., are highly polar.

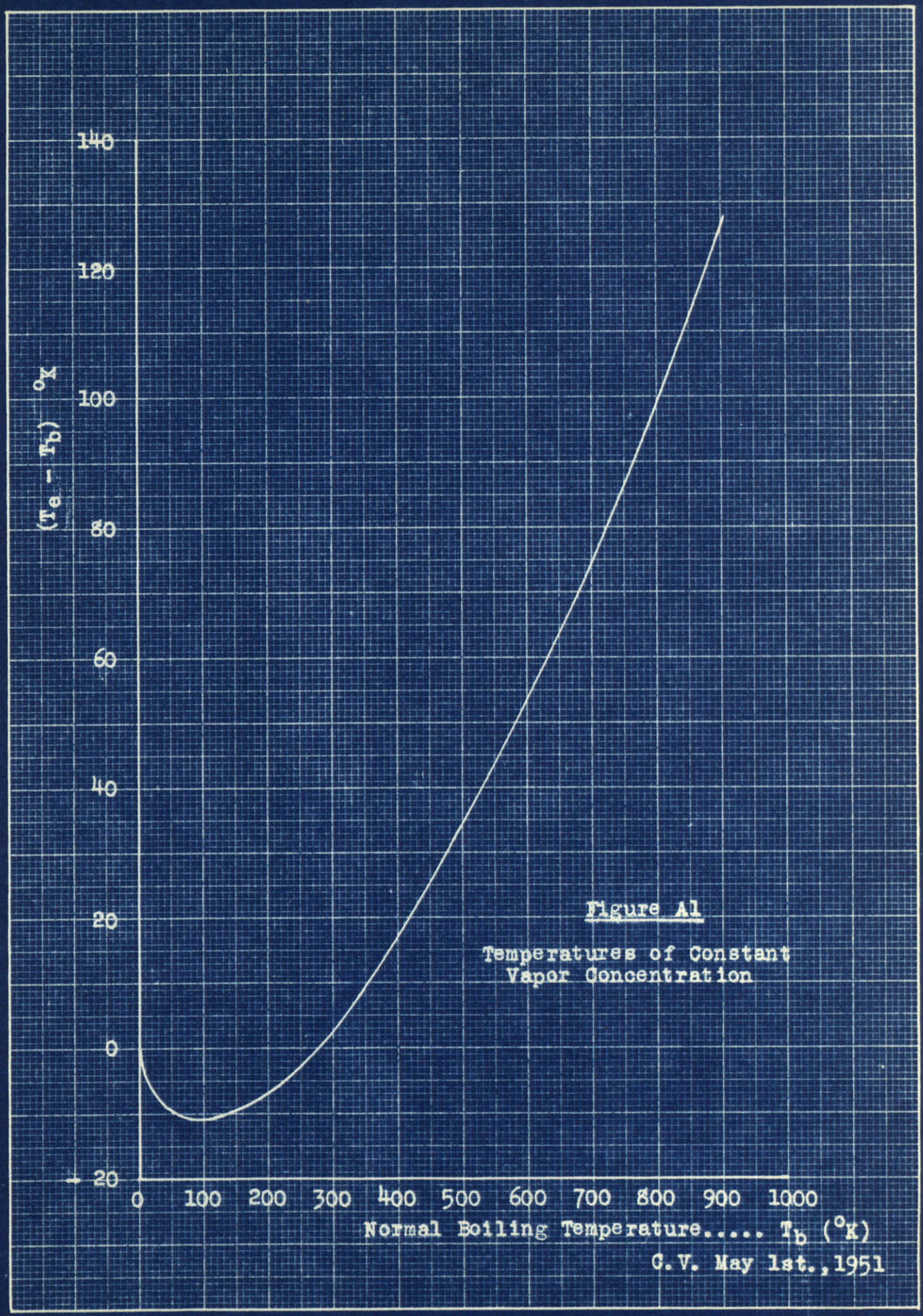

Figure A1

Temperatures of Constant Vapor Concentration

From a review of the pure hydrocarbons above the C3's for which reliable critical temperatures are known, Eaton (14) showed that:

$$t_c = 180 + 1.75\ a - 0.00088\ a^2 \qquad (A35)$$

where t_c = Critical temperature in °F
a = $(t_b + 100)s$
s = Specific Gravity at 60°F
t_b = 50% boiling point (A.S.T.M. Distillation)

This is shown to give a maximum deviation of 2% of the absolute critical temperature for the hydrocarbons tested.

Since the vapor pressure-temperature curves for all substances are similar in shape, it was suggested by Cox (12) that if a plot were devised on which a single reference substance were plotted as a straight line, then the vapor pressure plots of all other substances should be straight lines also. Thus, choosing steam as the reference substance and plotting vapor pressures as abscissae on a logarithmic scale, he drew a straight line at an angle of 30° to the log. P - axis and plotted the temperature scale as ordinates from this reference line from 70°F to 700°F using the vapor pressure-temperature data from the steam tables.

It was found that not only were the vapor pressure-temperature plots for other substances straight lines, even up to their critical points, but that for chemically related substances the lines all converged to a single point.

A further study of the Cox method of plotting was made by Calingaert and Davis (9) who found little curvature in lines plotted for widely different substances. Single points of convergence were found for the following groups:

(a) Paraffin Hydrocarbons
(b) Benzene monohalides
(c) Alcohols
(d) Silicon hydride series
(e) Metals

Thus to plot a complete vapor pressure-temperature line for any substance, it is only necessary to know either the corresponding vapor pressures and temperatures at two points or else to know them at one point together with the point of intersection of the vapor pressure-temperature curves of the group of which the substance in question is a member.

Edminster (16) showed that the Cox Chart may be used to predict critical temperatures and pressures. As stated above, the vapor pressure-temperature lines are found to be straight up to the critical point. If then for a given group of related compounds, the known experimental values of critical temperature and pressure are plotted and a curve drawn through these points, then the intersection of this curve with the vapor pressure-temperature lines of the other members of the group will give their respective critical temperatures and pressures.

Lewis (37) from a survey of the data suggested that:

$$\gamma = \left(\frac{T_c - \alpha}{M K}\right)^4 (D - d)^4 \qquad \text{(A36)}$$

from which:

$$\frac{T_c - \alpha}{K} = \frac{M \gamma^{1/4}}{D - d} = [P] \qquad \text{(A37)}$$

where $[P]$ = Parachor
γ = Surface Tension in dynes/cm.
D = Liquid density in grms/cc.
d = Vapor Density in grms/cc.
M = Molecular weight
α & K = Constants for groups of similar compounds containing the same number of atoms.

For a number of the groups, Lewis gives the constants shown in Table A3.

TABLE A3

Constants for Equation (A37)

Group	Equation
Inert Gases	$T_c = 3.7 \quad P - 48$
Halogens	$T_c = 5.57 \quad P - 188$
Halogen Acids	$T_c = 2.72 \quad P + 130$
Methyl Fluoride Group	$T_c = 3.43 \quad P + 39$
Ethyl Fluoride Group	$T_c = 3.21 \quad P + 20$
Fluorobenzene Group	$T_c = 2.33 \quad P + 63$

Wan (65) combined Lewis's relation for the critical temperature and an empirical relation by Samygin (58):

$$\gamma = (a\, r_\lambda + bD/M)^4 \qquad (A38)$$

where r_λ = Specific refraction corresponding to monochromatic light of wavelength λ.
D, M, and γ are as defined before.
a and b are constants

Assuming the vapor density, d, is small compared with the liquid density, D, this may be expressed:

$$[P] = a\,[R_\lambda] + b \qquad (A39)$$

where $[R_\lambda]$ = Molar refraction corresponding to monochromatic light of wavelength λ. $[R_\lambda] = M\, r_\lambda$.

He showed that:

$$T_c = K_1\,[R_\lambda] + K_2 \qquad (A40)$$

and split the 26 substances considered into six groups, the constantsof which are given in Table A4.

TABLE A4

Constants for Equation(A40)

Group	Equation
Hydrocarbons	$T_c = 7.02[R_\lambda] + 23.1$
Alcohols	$T_c = 6.74[R_\lambda] + 133.0$
Ethers	$T_c = 5.81[R_\lambda] + 67.1$
Carboxylic Acids	$T_c = 4.09[R_\lambda] + 268.5$
Esters	$T_c = 4.61[R_\lambda] + 150.8$
Nitrites	$T_c = 4.02[R_\lambda] + 228.4$

The correlation appears to be remarkably good giving results within 3% on the absolute scale and in most cases considerably higher accuracy than this.

In a further attempt to correlate the critical temperature with the parachor, Lewis (36) claims that for a homologous series:

$$\log [P] = (T_c + \alpha_c)/K_c = (T_b + \alpha_b)/K_b \qquad (A41)$$

where K_c and K_b are universal constants applicable to all the hydrocarbons and α_c and α_b are constants for a particular series but which increase with degree of unsaturation. Equation (A41) may be expressed:

$$T_c = K_c \log [P] - \alpha_c \qquad (A42)$$

$$T_b = K_b \log [P] - \alpha_b \qquad (A43)$$

and thus, by elimination of log [P]:

$$\frac{T_c + \alpha_c}{T_b + \alpha_b} = \frac{K_c}{K_b} \qquad (A44)$$

The equations given by Lewis are shown in Table A5.

TABLE A5

Constants for Equations (A42) and (A43)

Group	Equation
Paraffins Silicon series	$T_c = 551 \log [P] - 832$ $T_b = 416 \log [P] - 670$
Olefins	$T_c = 551 \log [P] - 824$ $T_b = 416 \log [P] - 664$
Acetylenes	$T_c = 551 \log [P] - 765$ $T_b = 416 \log [P] - 630$

From a list of twenty-two compounds of the groups considered in Table A5, the actual values of the ratio:

$$\frac{T_c + \alpha_c}{T_b + \alpha_b}$$

varied only between 1.308 for methane to 1.337 for propylene, the average value being 551/416 = 1.325.

Herzog (30) reviews Lewis's work and finds that an equation of the form:

$$T_c/T_b = a - b \log [P] \qquad (A45)$$

can be used to classify the critical temperatures of 140 compounds into only six groups. These are given in Table A6 together with the constants for each group.

TABLE A6

Constants for Equation (A45)

Compounds		n	Reliability	
Organic	Inorganic		Abs. 2s	Rel. %
Sat'd and unsat's hydrocarbons (acyclic and unsubstituted) a = 2.501 b = 0.4176	Paraffinic analogs, such as silicanes $1.29 < \frac{T_c}{T_b} < 1.70$	20	0.034	2.2
Aromatics and cyclics (substituted and unsubstituted) a = 2.640 b = 0.4634	$1.38 < \frac{T_c}{T_b} < 1.65$	28	0.082	5.4
Substituted aliphatics containing halogen and sulfur as fuctional groups a = 2.602 b = 0.4449	Inorganic halogen compounds $1.37 < \frac{T_c}{T_b} < 1.78$	26	0.075	4.7
Aliphatic esters, ethers, acetals, oxides	Some inorganic oxides and oxygen compounds such as SO_2, O_2 H_2O $1.35 < \frac{T_c}{T_b} < 1.64$	38	0.036	2.5
Aliphatic ketones, aldehydes, carboxyl acids and nitrogen compounds a = 2.301 b = 0.3548	Some inorganic nitrogen compounds such as N_2, N_2O, N_2O_4 $1.41 < \frac{T_c}{T_b} < 1.69$	23	0.067	4.4
Aliphatic alcohols and anhydrides a = 1.783 b = 0.1479	Inorganic "anhydrides", such as CO_2, H_2 $1.41 < \frac{T_c}{T_b} < 1.52$	14	0.033	2.3

In explanation of the table:

$$s = \left\{ \frac{\sum \left[(T_c/T_b)_{calc'd} - (T_c/T_b)_{exp'l} \right]^2}{(n - 2)} \right\}^{1/2}$$

n = Number of compounds considered
2s = a measure of the deviation to be expected in 95% of the cases.

The Relative Reliability of an experimental value is defined as:

$$\left(\frac{2\ s}{T_c/T_b} \right) 100\%$$

In giving the reliability for a group of compounds, the mean value of the ratio, $(T_c/T_b)_{mean}$, is used.

It should be noted that:

(1) The equations are based almost entirely on organic compounds for which good values of the parachor can be calculated. Inorganic compounds to which the equations are found to apply are indicated.

(2) For compounds falling into two or more groups, the average values from all equations concerned are recommended.

(3) All fluoromethanes and moderately substituted fluoroethanes can be estimated with greater accuracy from the equations for Aliphatic esters, etc. than for those given for hadogen-substituted aliphatics which give results for these compounds approximately 10% too high.

On the same basis, Herzog considered the equations of Meissner and Redding (44). For thirty-one compounds boiling below 235°K the equation:

$$T_c = 1.725\ T_b - 5.7 \qquad (A46)$$

gives a reliability of 12.8%. For ninety-three compounds (halogen and sulfur free) other than aromatics and naphthenes boiling over 235°K the equation:

$$T_c = 1.112\ T_b + 131.8 \qquad (A47)$$

gives a reliability of 5.4%.

The constants are slightly different than those that Meissner and Redding used so as to include a few inorganic compounds not included by the latter.

Meissner (43) gives a single equation which correlates the critical temperatures of over one hundred compounds to within 6.0%:

$$T_c = 20.2\ T_b^{0.6} - 143 - 1.2[P] + 10.4[R_D] + A \qquad (A48)$$

where $[R_D]$ = Molar refraction corresponding to monochromatic light of wave length of the Sodium D line.

A = Zero for hydrocarbons and halogen-substituted hydrocarbons
= 10.0 for all other compounds.

For hydrocarbons, a maximum error of 3% is encountered using this equation. Where values of T_b are not known, the equation:

$$T_b = (637\ [R_D]^{1.47} + B)/[P] \qquad (A49)$$

is suggested and values of the constant B are given for a number of groups in Table A7.

TABLE A7

Values of the Constant B for Equation (A49)

Group	B
Acids (monocarboxylic)	28,000
Alcohols (monohydroxy), including phenol, cresol, etc.	16,500
Amines, Primary	6,500
Secondary	2,000
Tertiary	- 3,000
Esters of monocarboxylic acids and monohydroxy alcohols	15,000
Ethers and mercaptans	4,000
Esters of dibasic acids and monohydroxy alcohols	30,000
Hydrocarbons acetylenic	- 500
Hydrocarbons aromatic	- 2,500
Hydrocarbons paraffinic and naphthenic	- 2,500
Hydrocarbons olefinic	- 4,500
Ketones	15,000
Monochlorinated normal paraffins	4,000
Nitriles	20,000

Gamson and Watson (21) point out that for a reduced temperature less than 0.65 and a pressure of less than ten atmospheres:

$$\omega = 0.1745 - 0.0838\ T_r \qquad (A50)$$

where ω = Expansion factor as defined for equation (A20) in the critical volume section.
T_r = Reduced temperature.

Thus, by combination of equations (A20) and (A50):

$$T_c = \frac{0.0838\ T}{0.1745 - V_1\omega_1/V} \qquad (A51)$$

where V = Molal volume at temperature T under conditions such that equation (A50) is applicable.

Since generalizations for $V_1\omega_1$ are available as given in equations (A22) and (A24), the critical temperature can be calculated from a reliable value of the molal volume.

(3) CRITICAL PRESSURES

Van der Waals (61) showed that if the reduced vapor pressure curves for all substances coincide, then:

$$\log (P_c/P) = \left\{(T_c/T) - 1\right\} \alpha \qquad (A52)$$

where P = Vapor pressure at Temperature T absolute units
α = Constant approximately = 3.0

Unfortunately the reduced vapor curves for all substances do not coincide and in fact:

$$1.5 < \alpha < 4.0$$

For hydrocarbons the use of the Cox Chart, as indicated by Edminster (16) can be used for the prediction of the critical pressure. However, as in the case of equation (A52), most predictions are in the form of equations in critical temperature or both critical temperature and critical volume.

Meissner and Redding (44) give the relation:

$$P_c = 20.8\ T_c/(V_c - 8) \qquad (A53)$$

With this equation it is stated that, using values of the critical temperature and volume predicted by equations (A29) and (A4) respectively, maximum errors of 11% are observed.

Wohl (68) and (69) proposes:

$$P_c = 21.8\ T_c/V_c \qquad (A54)$$

and Lautie (35):

$$P_c = (C\ [P]\ /V_c)^4 \qquad (A55)$$

this being a rearrangement of equation (A8).

Herzog (30) reviewing these equations shows that equation (A53) gives a reliability of 19.1% for all available data, though it is considerably better than this for hydrocarbons. Equation (A54) has a reliability of 18.1% and equation (A55) the very poor reliability of between 20 and 30% due to the fourth power involved.

The reliability has the same significance as in the cases of critical volume and critical temperature, i.e. $(2\ s/P_m)\ 100\%$ where

$$s = \left\{ \frac{\sum \left[(P_c)_{calc'd} - (P_c)_{exp'l} \right]^2}{(n-2)} \right\}^{1/2}$$

n = Number of compounds considered
2 s = a measure of the deviation to be expected in 95% of the cases.

He develops a formula from the general relationship:

$$\log (P/P_c) = m - n\ T_c/T \qquad (A56)$$

Thus at the normal boiling point:

$$-\log P_c = m - n\ T_c/T_b \qquad (A57)$$

Substituting equation (A45):

$$-\log P_c = m - n(a - b \log [P])$$

$$\text{or} \quad \log P_c = a' - b' \log [P] \qquad (A58)$$

where m, n, a, b, a' and b' are constants.

Analysis of over one hundred compounds showed that equation (A58) could be successfully fitted into six groups as shown in Table A8.

TABLE A8

Groups covered and constants for Equation (A58)

Group of compounds	Constants	n	Mean log P_c	Reliability	
				Abs	%
Sat'd and unsat'd hydrocarbons (acyclic and unsubstituted) including methane.	a'=3.0477 b'=0.6528	18	1.503	0.035	8.4
Aromatics and cyclics, excluding biphenyls and condensed ring systems.	a'=3.8584 b'=0.9215	25	1.622	0.10	26.0
Aliphatic amines, esters, halogen and sulfur compounds (excluding CH_3F, and CS_2), inorganic halogen and sulfur compounds (excluding F_2) and NH_3.	a'=3.4271 b'=0.7829	45	1.664	0.07	18.0

TABLE A8 (cont)

Group of compounds	Constants	n	Mean log P_c	Reliability	
				Abs	%
Aliphatic acids, alcohols and anhydrides.	a'=2.9929 b'=0.5718	8	1.746	0.036	8.6
Aliphatic ethers and ketones	a'=3.3777 b'=0.7810	5	1.617	0.024	5.7
Aliphatic nitriles and HCN	a'=2.6387 b'=0.4627	4	1.594	0.006	1.4

Gamson and Watson (21) give a plot of Critical Pressure versus Number of Carbon Atoms in the Molecule for the Paraffin Hydrocarbons and show that for any other group of compounds:

$$P_c = P_c' + \Delta P/(n + C) \qquad (A59)$$

where P_c' = Critical pressure for the paraffin hydrocarbon corresponding to n.
n = Number of carbon atoms in the molecule.
ΔP and C = Constants given in Table A9 for a number of groups.

TABLE A9

Constants for Equation (A59)

Group	ΔP lbs./sq. in	C
Acids	300	0
Alcohols	480	0
Aldehydes	250	0
Amines: Primary	69	- 1.3
Secondary	80	0
Aromatic Hydrocarbons monocyclic	830	- 3
Esters	60	- 1.6
Ethers	0	0
Monohalogenated paraffins	47	- 1.0
Ketones	180	0
Naphthenes	970	0
Nitriles	0	0
Phenols	1360	- 3
Mono-olefins	63	0

Meissner (43) pursuing the policy of giving a single relationship that can be used for all compounds proposes:

$$P_c = \frac{60.3\ T_c}{1.5[P] + 9 - 4.34[R_D]^{1.226}} \qquad (A60)$$

where $[R_D]$ = Molar refraction corresponding to light of the Sodium D line

$[P]$ = Parachor

The precision to be expected on the critical pressure predicted by this equation depends to some extent on the accuracy of the value of the critical temperature available. Using values of this latter as predicted by equation (A48), a maximum error of 15% is shown except for acetic acid, acetonitrile, methanol and carbon disulfide. It appears that the success of equation (A60) is poorest with the first members of a series and that it improves with the higher members.

APPENDIX D: PARACHOR AND MOLAR REFRACTION VALUES FOR ATOMIC AND STRUCTURAL ELEMENTS

The following Table A10 gives a selection of the atomic and structural parachors presented by Mumford and Phillips, (47), and the corresponding molar refractions presented by Fajans, (17).

TABLE A10

	Molar Refraction (Sodium D Line)	Parachor
C	2.418	9.2
H	1.100	15.4*
CH_2	4.618	40.0
O (hydroxyl)	1.525	20
O (ether)	1.643	20
O (carboxyl)	2.211**	39 **
F	-	25.5
Cl	5.967	55
Br	8.865	69
I	13.90	90
N (primary amine)	2.322	17.5
N (secondary amine)	2.502	17.5
N (tertiary amine)	2.840	17.5
N (nitrile)	5.516***	55.5***
S	-	50.
P	-	40.5
3-Membered ring	0	12.5
4-Membered ring	0	6.0
5-Membered ring	0	3
6-Membered ring	0	0.8
7-Membered ring	0	- 4.0
Double bond	1.733	19.0
Semi-Polar double bond	1.733	0
Triple bond	2.398	38
Singlet linkage	-	- 9.5

* Hydrogen on Bromine has a parachor of 16.4; on Oxygen of 10; and on Nitrogen of 12.5.
** Includes allowance for double bond.
*** Includes allowance for triple bond.

APPENDIX E: METHOD OF LEAST SQUARES FOR OBTAINING THE BEST STRAIGHT LINE THROUGH EXPERIMENTAL DATA

Assuming that the experimental points are plotted on rectangular co-ordinates (x, y), then the equation of a straight line is:

$$y = A\,x + B$$

Let the experimental points be (X, Y). The deviation of any point from the line will thus be:

$$\Delta = Y - y = Y - (AX + B)$$

By the method of least squares $\Sigma\Delta^2$ is made a minimum:

$$\Sigma\Delta^2 = \Sigma\left\{Y^2 + A^2X^2 + B^2 + 2AXB - 2Y(AX + B)\right\}$$

For this to be a minimum:

$$\frac{\partial(\Sigma\Delta^2)}{\partial A} = \Sigma\,(2AX^2 + 2BX - 2XY) = 0$$

$$\frac{\partial(\Sigma\Delta^2)}{\partial B} = \Sigma\,(2B + 2AX - 2Y) = 0$$

or

$$2A\Sigma X^2 + 2B\Sigma X - 2\Sigma XY = 0$$

$$\Sigma 2B + 2A\Sigma X - 2\Sigma Y = 0$$

For the case of critical temperatures:

X represents n, the number of carbon atoms
Y represents the ratio T_b/T_c

and for the paraffin hydrocarbons:

X	X^2	Y	XY
1	1	0.5863	0.5863
2	4	0.6056	1.2112
3	9	0.6178	1.8534
4	16	0.6439	2.5756
5	25	0.6577	3.2885
7	49	0.6847	4.7929
9	81	0.7111	6.3999
10	100	0.7409	7.4090
$\Sigma X=41$	$\Sigma X^2=285$	$\Sigma Y=5.2480$	$\Sigma XY=28.1168$

Therefore $A\ 285 + B\ 41 - 28.1168 = 0$

$B\ 8 + A\ 41 - 5.2480 = 0$

from which $A = 0.0158 = C + 2H$

$B = 0.5750 = 2H$

Hence the value for the carbon atom = $\underline{C = -0.5592}$

and the value for the hydrogen atom = $\underline{H = 0.2875}$

APPENDIX F: LIST OF SYMBOLS

Br	Atomic Value for Bromine
C	Atomic Value for Carbon
Cl	Atomic Value for Chlorine
D	Saturated liquid density (grms/cc)
D_c	Critical Density (grms/cc)
D_s	Density of Saturated liquid at the normal boiling point (grms/cc)
D_{cc}	Carbon to carbon double bond value
D_{co}	Carbon to oxygen double bond value
D_{cs}	Carbon to sulfur double bond value
D_{so}	Sulfur to oxygen double bond value
F	Number of Fluorine atoms in a molecule
F	Atomic value of Fluorine
H	Atomic value of hydrogen
M	Molecular weight
I	Atomic value of iodine
N	Atomic value of nitrogen
O	Atomic value of oxygen
(OH)	Atomic value of hydroxyl group
P	Vapor pressure
P_c	Critical pressure (atmos.)
P_r	Reduced pressure
$[P]$	Parachor
$[R_D]$	Molar refraction corresponding to monochromatic light of wave-length of the Sodium D line
$[R_\lambda]$	Molar refraction corresponding to monochromatic light of wave length λ
R	Gas constant
R_6	Atomic value of a six-membered ring
S	Atomic value of sulfur
T	Absolute temperature (°K)
T_c	Critical temperature (°K)
T_r	Reduced temperature
T_b	Normal boiling temperature (°K)

T_e	Temperature of liquid whose saturated vapor occupies 22.4 liters per grm mol (°K)
T_m	Normal melting point (°K)
T_{cc}	Carbon to carbon triple bond value
T_{cn}	Carbon to nitrogen triple bond value
T_{nn}	Nitrogen to nitrogen triple bond value
(X, Y)	Rectangular co-ordinates of an experimental point
d	Saturated vapor density (grms/cc)
m	Number of carbon atoms in molecule
n	Number of carbon atoms in molecule
n_c	Number of carbon atoms in molecule
n_λ	Refractive index measured with monochromatic light of wave-length λ
r	Ratio of non-cyclic carbon atoms to the total number of carbon atoms in the molecule
r_λ	Specific refraction corresponding to monochromatic light of wave-length λ
s	Specific gravity at 60°F
t_b	50% boiling point (A.S.T.M. distillation)
t_c	Critical temperature (°F)
v	Molal volume (ccs/grm. mol)
(x, y)	Rectangular co-ordinates of a predicted point
γ	Surface tension (dynes/cm)
Δ	Deviation between experimental and predicted value
λ	Wave-length of monochromatic light
Σ	Summation of

Throughout the work, A, B, C, D, K and α have been used for sundry constants.

APPENDIX G: LITERATURE CITATIONS

(1) Altschul, Z. phys. Chem., 11, 590, (1893)

(2) Beattie, J. Phys. Chem., 3, 96-97, (1935)

(3) Beattie, J. Am. Chem. Soc., 61, 24-27, (1939)

(4) Beilstein, "Handbuch der Organischen Chemie", Vol. 1, V, IV Edn.

(5) Berthaud, J. de chim. phys., 15, 3, (1917)

(6) Berthaud and Brum, J. de chim. phys., 21, 143, (1924)

(7) Brown, J. Chem. Soc. (London), 89, 311, (1906)

(8) Cailletet and Mathias, Comptes rendus, 102, May 1886, 104, June 1887

(9) Calingaert and Davies, Ind. Eng. Chem., 17, 1287, (1925)

(10) Coffin and Maass, J. Am. Chem. Soc., 50, 1427, (1928)

(11) Cork, Rev. Sci. Instr., 1, 563, (1930)

(12) Cox, Ind. Eng. Chem., 15, 592, (1923)

(13) de Heen, "Recherches, Partie Experimentale", p102, Paris, (1888)

(14) Eaton, Ind. Eng. Chem., 24, 819, (1932)

(15) Edgar, J. Am. Chem. Soc., 51, 1540-1550, (1929)

(16) Edminster, Oil Gas J., 22, (7/2/31)

(17) Fajans, "Physical Methods of Organic Chemistry" pp. 672-83, Inter Science Publishers Inc., New York, (1945)

(18) Ferguson, Nature, 125, 597, (1930)

(19) Ferguson and Kennedy, Nature, 125, 1479, (1930)

(20) Ferretto, Ann. chim. phys., 30 I, 296, (1900)

(21) Gamson and Watson, Nat'l Pet'm News, 36, R 258-264, (1939) ? (1944)

(22) Germann and Taylor, J. Am. Chem. Soc., 48, 1154, (1926)

(23) Gibling, J. Chem. Soc., 299-309, (1941)
661-666, (1942)
146-153, (1943)

(24) Guldberg, Z. Physik. Chem., 5, 134, (1880)

(25) Guye, Arch. Sc. phys. nat. Geneve, (4) 3, 274 (1901)
Zeutre, 1, 1314, (1902)

(26) Guye and Mallet, Arch. Sc. phys. nat. Geneve, 13, pp. 13, 129, 274, 462, (1902)

(27) "Handbook of Butane - Propane Gases", 2nd Edn. p. 14, (1935)

(28) Hackspill and Mathieu, Bull. de la Soc. chim. de France, 25, 482, (1919)

(29) Herz and Neukirch, Z. phys. Chem., 104, 433, (1923)

(30) Herzog, Ind. Eng. Chem., 36, 997-1001, (1944)

(31) Hollmann, Z. phys. Chem., (Stoch und Ver.) 43, 129 (1903)

(32) I. C. T., Vol. III, p.248

(33) Landolt-Boernstein Physikalisch-chemische Tabellen, 5th Edn., Vol IIa, J. Springer, Berlin (1923)

(34) Lange, "Handbook of Chemistry", 1934 Edn.

(35) Lautie, Bull. soc. chim., (5)3, 1689, (1936)

(36) Lewis, (a) Nature, 145, 551, (1940)
(b) J. Chem. Soc., 1056, (1938)

(37) Lewis, J. Chem. Soc., 261-264, (1938)

(38) Lorentz and Lorenz, see Daniels "Outlines of Physical Chemistry" Page 69, Wiley (1948)

(39) Maass and Boomer, J. Am. Chem. Soc., 44, 1709, (1922)

(40) Mathias, "Le Point Critique des Corps Purs", p.164, (1916)

(41) McKee and Parker, Ind. Eng. Chem., 20, 1169, (1928)

(42) Maxwell, "Data Book on Hydrocarbons", D. van Nostrand Co. Inc., New York, (1950)

(43) Meissner, Chem. Eng. Prog., 45, No. 2, (Feb. 1949)

(44) Meissner and Redding, Ind. Eng. Chem., 34, 521-526, (1942)

(45) Morehouse, Can. J. Res., 5, 306-312, (1931)

(46) Morehouse, Can. J. Res., 11, 640, (1934)

(47) Mumford and Phillips, J. Chem. Soc., 131, 2112-2133, (1929)

(48) Nadejdine, J. Russ., 14, 157, 536, (1882)
15, 25, (1883)

(49) Nadejdine, Rep. Exp. Phys., 23, 617, (1887)

(50) Nelson, Oil Gas J., p. 46 - 11/26/36
52 - 1/ 7/37
39 - 2/ 4/37
60 - 2/18/37
46 - 3/18/37
38 - 4/ 1/37
161 - 5/27/37

(51) Paterno and Mazzucchelli, Gazetta chimica italiana, 50 I, 30, (1920)

(52) Pawlewski, Ber., 16, 2632, (1883); Ber., 21, 2141 (1888)

(53) Pawlewski, Ber., 15, 2460, (1882)

(54) Perry, "Chemical Engineers' Handbook", Rev. 3rd Edn. (1950)

(55) Pickering, Bureau Standards' Sci. Paper 541, (1926)
J. Phys. Chem., 28, 97-124, (1924)

(56) Prud'homme, J. chim. phys., 94, 270, 307, (1920)

(57) Prud'homme, J. chim. phys., 21, 243-246, (1924)

(58) Samygin, J. Phys. Chem. (U.S.S.R.), 10, 455, (1937)

(59) Sugden, "The Parachor and Valency", (London), Routledge and Sons, (1930)

(60) Ter Gazarian, J. de chim. phys., 4, 140, (1906)

(61) Van der Waals, "Kontinuitat des Gas fornigen und flussigen Zustandes", Leipzig, (1899)

(62) Vespignani, Gaz. chim. italiana, 33 I, 73, (1903)

(63) Vincent and Chappius, "Comptes ----- l'ac. Sci., (France) 101, 427, (1885), 103, 379, (1886)

(64) Walden, Z. phys. Chem., 65, 108-205, 257-277, (1909)

(65) Wan, J. Phys. Chem., 45, 903-907, (1941)

(66) Watson, Ind. Eng. Chem., 23, 360, (1931)

(67) Watson, Ind. Eng. Chem., 35, 398, (1943)

(68) Wohl, Z. physik. Chem., 99, 207, (1927)

(69) Wohl, Z. physik. Chem., 87, 1, (1914)

(70) Young, Trans. Roy. Soc., (Dublin), 12, 374-432, (1910)

(71) Young, Phil. Mag., 33, 153, (1892)

(72) Young, J. Chem. Soc., (London), 63, 1191, (1893)

(73) Zhuravlev, J. Phys. Chem., (Russ.), 9, 875-882, (1937)